

Site: <u>New Bedier</u> d Break: <u>5.4</u> Other: <u>5/87/</u>

R-31-5-4-6 NB-*06*-GW-F

INVENTORY OF GROUNDWATER RESOURCES

NEW BEDFORD HARBOR STUDY BRISTOL COUNTY, MASSACHUSETTS

EPA WORK ASSIGNMENT
NUMBER 28-1L43
CONTRACT NUMBER 68-01-6699

NUS PROJECT NUMBER S725

JUNE 1986



Park West Two Cliff Mine Road Pittsburgh, PA 15275 412-788-1080

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SUBMITTED FOR NUS BY:

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CONTENTS

SECTION		
1.0 1.1 1.2 1.3	INTRODUCTION PURPOSE AND SCOPE OF WORK SOURCES OF DATA PHYSIOGRAPHY, CLIMATE, AND LAND USE	1-1 1-1 1-2 1-4
2.0	GENERAL GEOLOGY AND HYDROLOGY	2-1
3.0 3.1 3.2	OCCURRENCE OF GROUNDWATER GENERAL PRINCIPLES OCCURRENCE OF GROUNDWATER IN UNCONSOLIDATED DEPOSITS	3-1 3-1 3-4
3.3 3.4	OCCURRENCE OF GROUNDWATER IN BEDROCK GROUNDWATER MOVEMENT AND PUMPING EFFECTS	3-14 3-19
4.0 4.1 4.2 5.0 5.1 5.2 5.3	MAJOR WATER SUPPLIES SURFACE WATER SUPPLIES GROUNDWATER SUPPLIES WATER QUALITY IN THE STUDY AREA INFLUENCES ON NATURAL WATER QUALITY GENERAL WATER QUALITY CHARACTERISTICS IN THE STUDY AREA KNOWN AND/OR SUSPECTED CONTAMINATION PROBLEMS	4-1 4-1 4-4 5-1 5-1 5-2 5-3
REFERE	NCES	R-1
APPEND	DICES	
Α	MASSACHUSETTS DRINKING WATER QUALITY REGULATIONS,	A-1

TABLES

NUMBER		<u>PAGE</u>
3-1	ESTIMATED HYDRAULIC CONDUCTIVITY OF DEPOSITS IN STUDY AREA	3-3
3-2	ESTIMATED AQUIFER CHARACTERISTICS-MUNICIPAL WELL SITES	3-15
4-1	MUNICIPAL WATER SUPPLY STATISTICS	4-2
A-1	MASSACHUSETTS MAXIMUM CONTAMINANT LEVELS FOR INORGANICS REGULATION 310 CMR 22.06	A-4
A-2	MASSACHUSETTS MAXIMUM CONTAMINANT LEVELS FOR CHLORINATED HYDROCARBON AND CHLOROPHENOXY PESTICIDES REGULATION 310 CMR 22.07	A-5
A-3	MASSACHUSETTS MAXIMUM CONTAMINANT LEVELS FOR TRIHALOMETHANES, TURBIDITY, RADIONUCLIDES REGULATIONS 310 CMR 22.08, 22.09	A-6

FIGURES

NUMBER		<u>PAGE</u>
1-1	STUDY AREA	1-3
2-1	BEDROCK GEOLOGY OF THE NEW BEDFORD AREA	2-2
2-2	APPROXIMATE BEDROCK SURFACE ELEVATIONS	
Α	ASSAWOMPSET POND QUADRANGLE	2-3
В	SNIPATUIT POND QUADRANGLE	2-4
С	FALL RIVER EAST QUADRANGLE	2-5
D	NEW BEDFORD NORTH QUADRANGLE	2-6
Ε	MARION QUADRANGLE	2-7
F	WESTPORT QUADRANGLE	2-8
G	NEW BEDFORD SOUTH QUADRANGLE	2-9
н	SCONTICUT NECK QUADRANGLE	2-10
2-3	SURFICIAL GEOLOGY OF STUDY AREA	
Α	ASSAWOMPSET POND QUADRANGLE	2-12
В	SNIPATUIT POND QUADRANGLE	2-13
С	FALL RIVER EAST QUADRANGLE	2-14
D	NEW BEDFORD NORTH QUADRANGLE	2-15
Ε	MARION QUADRANGLE	2-16
F	WESTPORT QUADRANGLE	2-17
G	NEW BEDFORD SOUTH QUADRANGLE	2-18
Н	SCONTICUT NECK QUADRANGLE	2-19

FIGURES (CONTINUED)

NUMBER		PAGE
3-1 APPROXIMATE TRANSMISSIVITIES OF		
	UNCONSOLIDATED DEPOSIT	
Α	ASSAWOMPSET POND QUANDRANGLE	3-5
В	SNIPATUIT POND	3-6
С	FALL RIVER EAST	3-7
D	NEW BEDFORD NORTH	3-8
Ε	MARION	3-9
F	WESTPORT	3-10
G	NEW BEDFORD SOUTH	3-11
4-1	LOCATION OF DARTMOUTH ROUTE 6 WELL AND MONITORING WELL FIELD	4-6
	MONTORING WELL FIELD	

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1.0 INTRODUCTION

The United States Environmental Protection Agency (EPA), under authority promulgated by the Comprehensive Environmental Response, Compensation, and Liability Act (i.e., the Superfund act), assigned the New Bedford Site in Bristol County, Massachusetts, to its National Priorities List of hazardous waste sites in July 1981. This assignment qualified the site for monies and resources created by the Superfund act. The New Bedford Site was so assigned because the widespread presence of polychlorinated biphenyls (PCBs) in the New Bedford Harbor and surrounding areas poses a threat to the public health, public welfare, and environment. The site has been designed by the Commonwealth of Massachusetts as its highest priority uncontrolled hazardous waste site.

Under EPA Work Assignment No. 28-1L43, issued on August 24, 1983, the Remedial Planning Office of NUS Corporation (NUS) was authorized to implement a remedial action program for the New Bedford Site.

The overall objective of the remedial action program was to attenuate the release of contaminants from various sources and sites to a level that was consistent with the protection of public health, safety, and welfare. This objective incompasses the protection of the surface water, groundwater, air, and terrestrial resources of the regional environment. Part of the remedial action program included a number of regional and site-specific investigations to characterize the local and regional environmental settings. Results of these investigations will be used in subsequent feasibility studies on how to remediate the contamination problems.

The objective of one of the regional studies was to investigate the hydrogeology of the region using existing information. This report presents the results of this investigation.

1.1 Purpose and Scope of Work

The hydrogeologic inventory of groundwater resources for the New Bedford Site involves both the development of a regional hydrogeologic scenario and the

evaluation and assessment of potential contaminant impacts on critical groundwater resources. The purpose of this report is to provide a compendium of groundwater resources to be used as a reference document in the decision-making process and for planning future groundwater studies. The report may be updated as information becomes available from future investigations.

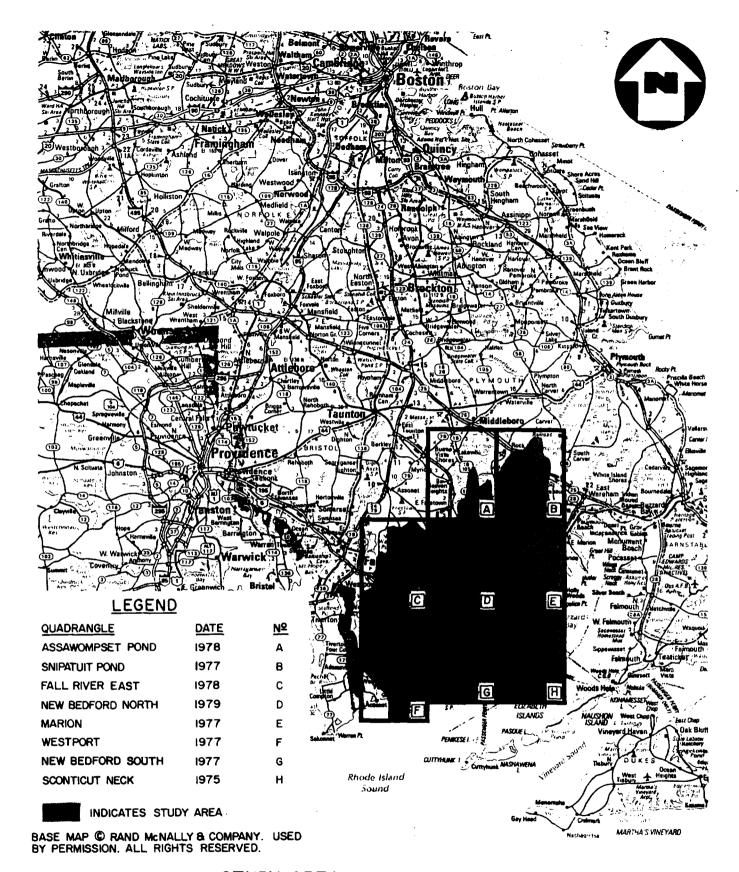
The area of interest includes the watershed of Buzzard's Bay, including the towns of New Bedford, Acushnet, Fairhaven, Dartmouth, Mattapoisett, Marion, Westport, Fall River, Rochester, and the southern portion of Freetown. Figure 1–1 highlights the study area. This figure also includes an index showing how the accompanying figures are arranged.

The inventory involves the compilation of available data on the hydrogeology, quality, and use of the groundwater resources in the study area. Information of bedrock type and water-bearing characteristics is presented. The extent and characteristics of the surficial, unconsolidated deposits are also discussed. In particular, the geomorphology, lithologies, and water-bearing characteristics are detailed, as are the interrelationships of groundwater flow between the lithologic units. Groundwater flow patterns are also presented.

1.2 Sources of Data

Information on the bedrock and surficial geology, as well as the corresponding water-bearing characteristics, was compiled from several engineering consultant's reports along with published and unpublished data from the United States Geological Survey (USGS). Of particular value was a report published by the USGS on the Groundwater Resources of the Mattapoisett River Valley Aquifer in Plymouth County and a report by Geoscience, Inc.

In general, less information than expected was obtained even though appropriate personnel were contacted and a thorough search was made of agency files and previous studies completed by others. This scarcity of information reflects not only a lack of groundwater use in many communities (e.g., New Bedford) but also the lack of mineral reserves in the New Bedford area that would lead to subsurface



STUDY AREA
HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES

NEW BEDFORD, MASSACHUSETTS

SCALE: I"= 9.1 miles



investigations and related engineering studies. The predominance of granitic bedrock with a relatively thin overburden does not, in effect, demand extensive geologic and geotechnical considerations for most actions.

Information on municipal water systems and representative domestic supplies was derived from contacts with municipal water authorities and zoning departments, the Massachusetts Water Resources Commission, the Massachusetts Department of Environmental Quality Engineering (DEQE), engineering consultant reports, and the USGS.

The literature search also involved the compilation of readily available water quality data for public and private sources, with special attention on organic constituents. Representative analyses were obtained from municipal water authorities, engineering consultants reports, the Water Supply Division of DEQE, and the USGS. Areas of known water quality problems are discussed in Section 5.3.

1.3 Physiography, Climate, and Land Use

The study area is located in the Coastal Lowlands Physiographic Province of New England. The present topography is a product of physical and chemical erosion, with subsequent glacial erosion and deposition. Topographic features, which include streams, harbors and hills, have a general northwest trend. Land surface elevations range from sea level to about 240 feet. The surface topography is composed of smooth hills, with intervening valleys; southward sloping, low-rolling plains; and flat, low-lying wetlands.

The climate of the study area is characterized by warm summers and relatively mild, wet winters, with the rainfall in the area fairly evenly distributed throughout the year. The average yearly precipitation measured in Dartmouth is 41 inches (Geoscience, 1980), with 48.7 inches measured in Rochester (Olimpio, deLima, 1984). Free-water surface evapotranspiration takes place from May to September (Olimpio, deLima, 1984). The temperature varies from an average low of about 32° in January to about 72° in July (Geoscience, 1980).

Land use in the study area includes agricultural and forest land, urban development, and light industry. Most of the urban and industrial areas are located in the southern part of the study area, mainly in the communities of New Bedford, Fairhaven, and Fall River. The projected development of land by 2020, according to the New England River Basins Commission, shows a 50 percent increase in urban area, largely as a result of light industrial development (Olimpio, deLima, 1984). A small population increase is also projected.

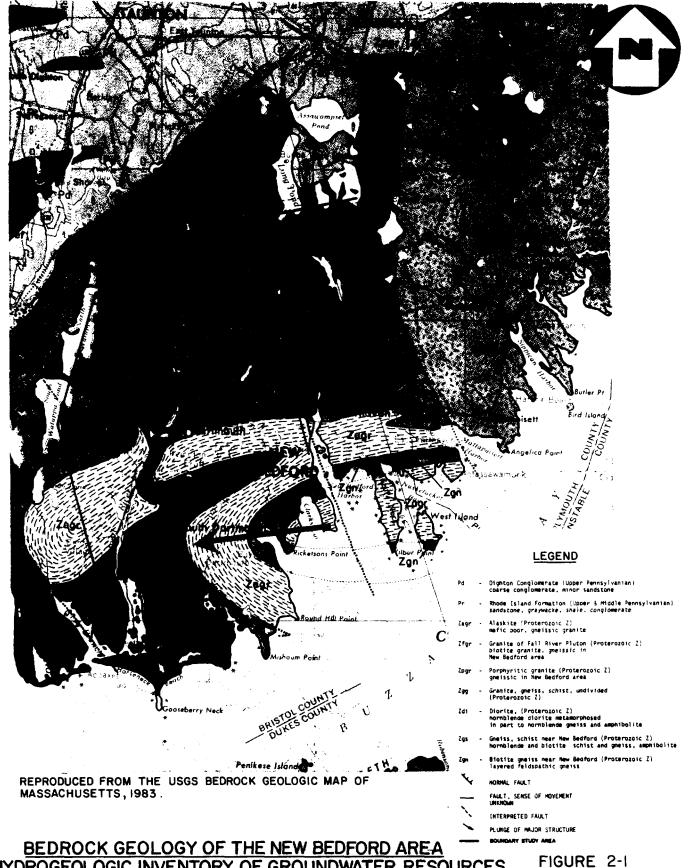
2.0 GENERAL GEOLOGY AND HYDROLOGY

Figure 2-1 presents the bedrock and major structural features of the New Bedford study area. The study area is underlain by Precambrian (older than 600 million years ago) plutonic, intrusive, and metamorphic rocks. Major rock types include granite, biotite granite, granitic gneiss, gneiss, schist, and diorite. These rocks are modestly deformed and highly faulted in areas.

As shown on the figure, several major faults and interpreted faults have been mapped in the vicinity. However, the direction and extent of movement of the fault blocks in many cases is unknown. Faulting sometimes causes weaker zones to develop in the bedrock, which then erode easier than surrounding areas. In many cases, watercourses reflect these areas where water flows along the path of least resistance. As mentioned before, the geomorphic features in the region of Buzzard's Bay indicate a north-trending lineation in the underlying bedrock. Examples of these features include the Acushnet and Westport Rivers, New Bedford Harbor, and the intervening highlands.

As seen on Figures 2-2A through 2-2H, which have been developed from an unpublished map of a portion of the study area completed by the USGS, the topographic bedrock surface is highly variable owing to repeated glacial activities during the Pleistocene Epoch which ended 10,000-15,000 years ago. The bedrock topography and surficial deposits existing today are a product of the last period of glaciation, the Wisconsinan.

The moving ice sheets scoured, plucked, and excavated the bedrock surfaces, widening and deepening existing bedrock valleys. The glacial ice deposited material either directly upon the bedrock surface or indirectly by meltwater from the ice. These glacial deposits, by obscuring the bedrock and filling in bedrock depressions, have formed the existing surface, which now has a smoother topography.

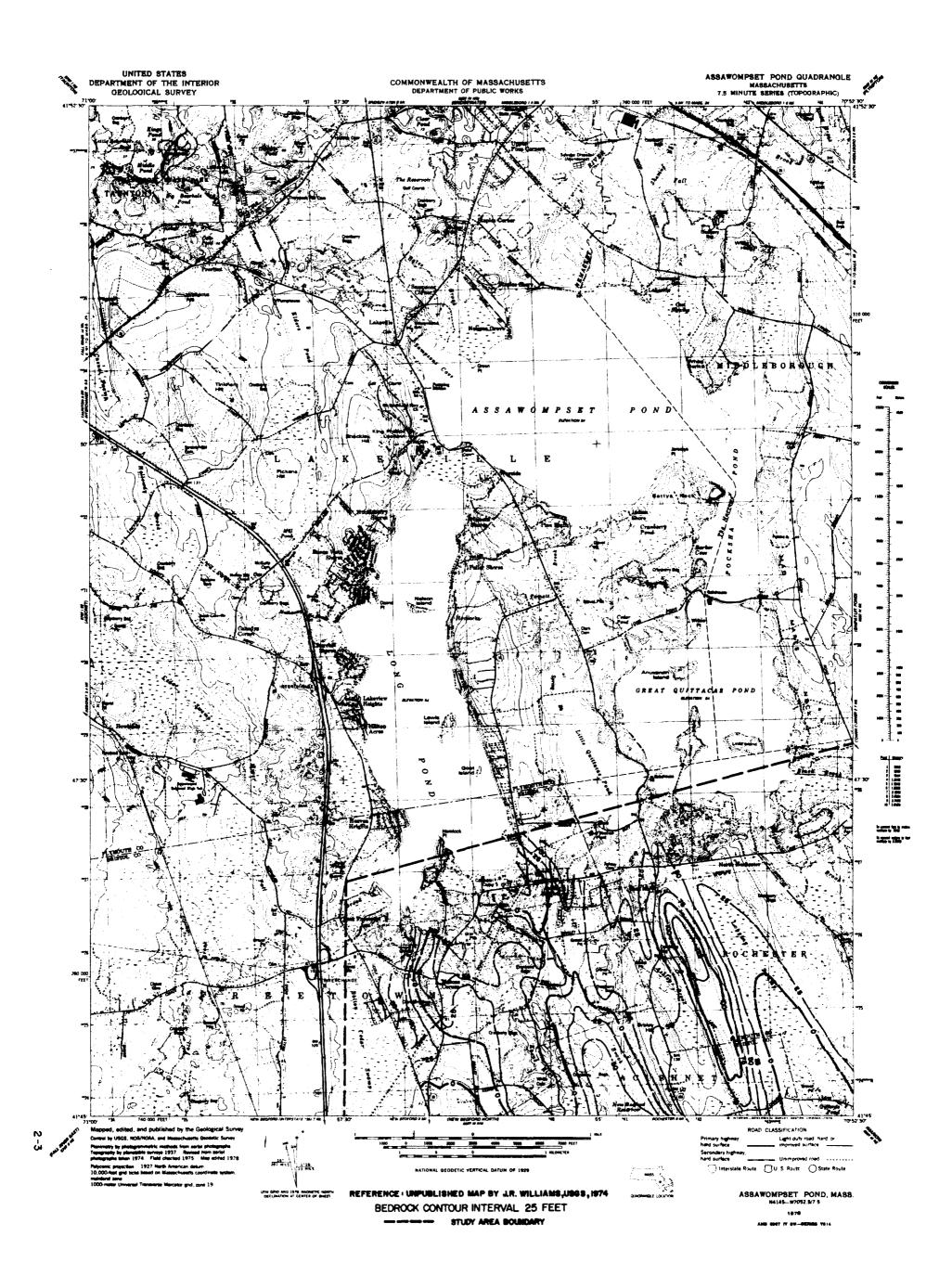


HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES

NEW BEDFORD HARBOR STUDY NEW BEDFORD, MASSACHUSETTS

SCALE I" APPROXIMATELY 4 MILES





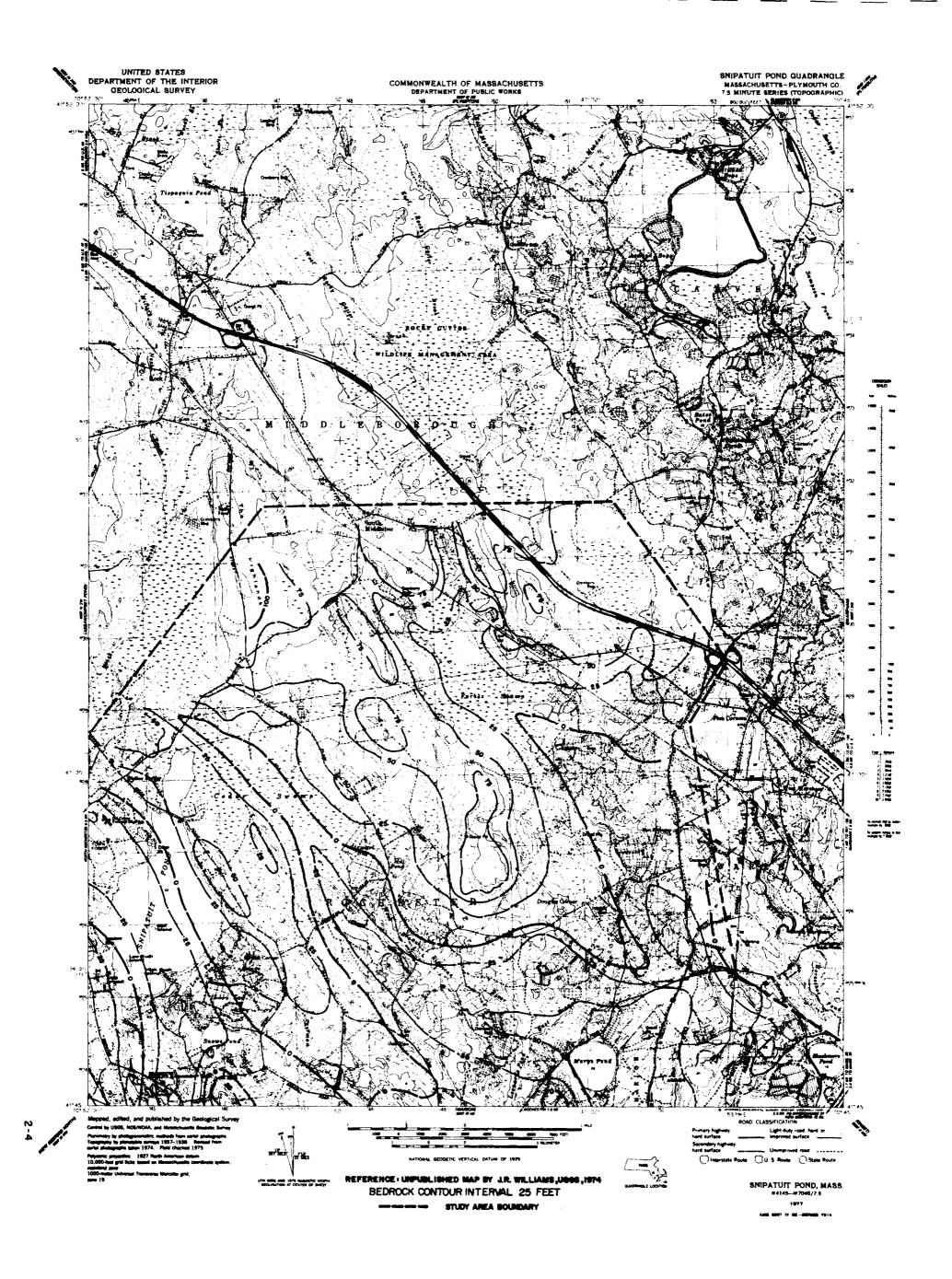
APPROXIMATE BEDROCK SURFACE ELEVATIONS

ASSAWOMPSET POND QUADRANGLE

HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

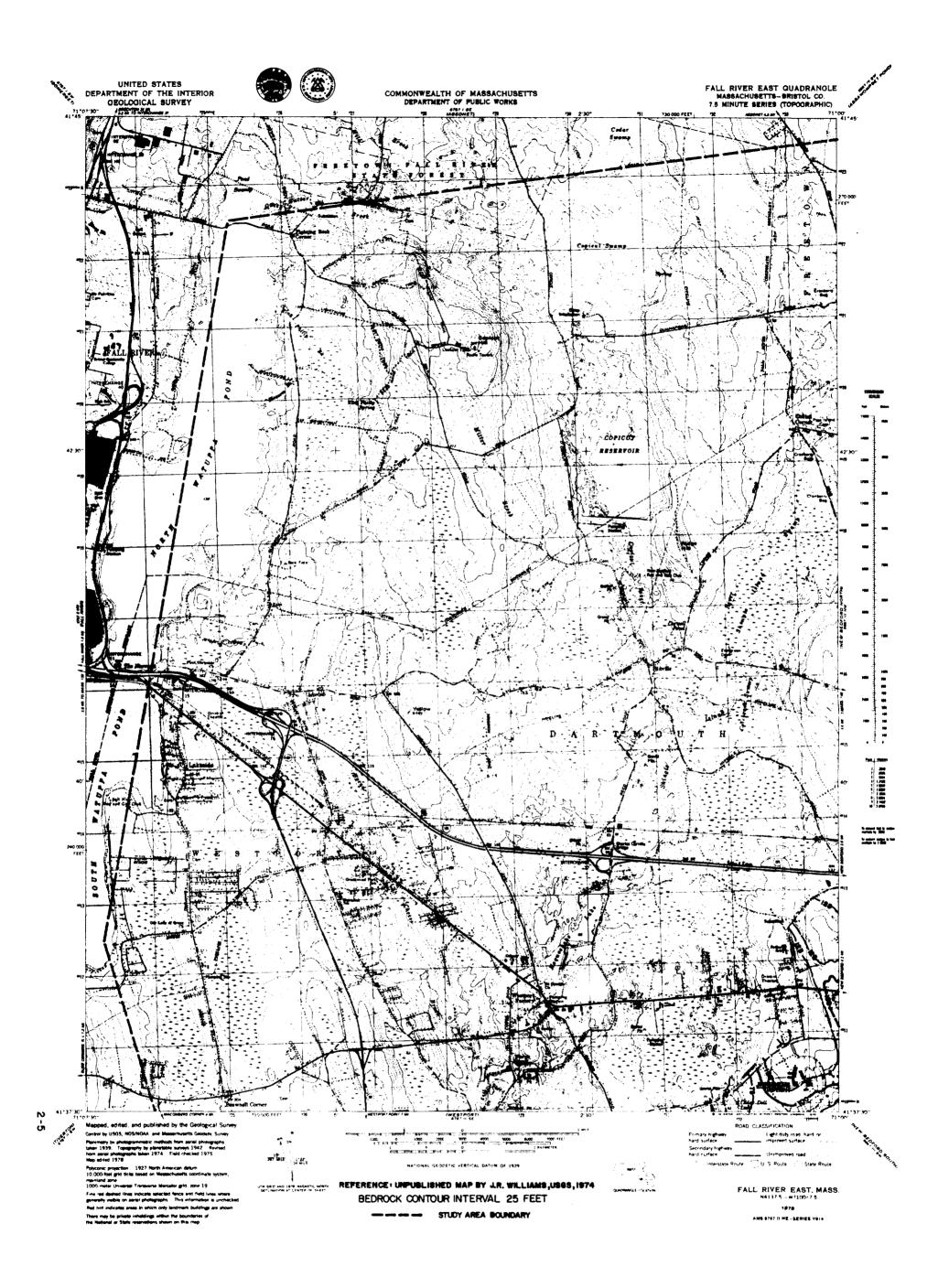
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA





APPROXIMATE BEDROCK SURFACE ELEVATIONS
SNIPATUIT POND QUADRANGLE
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA
SCALE I"= 4000'





APPROXIMATE BEDROCK SURFACE ELEVATIONS

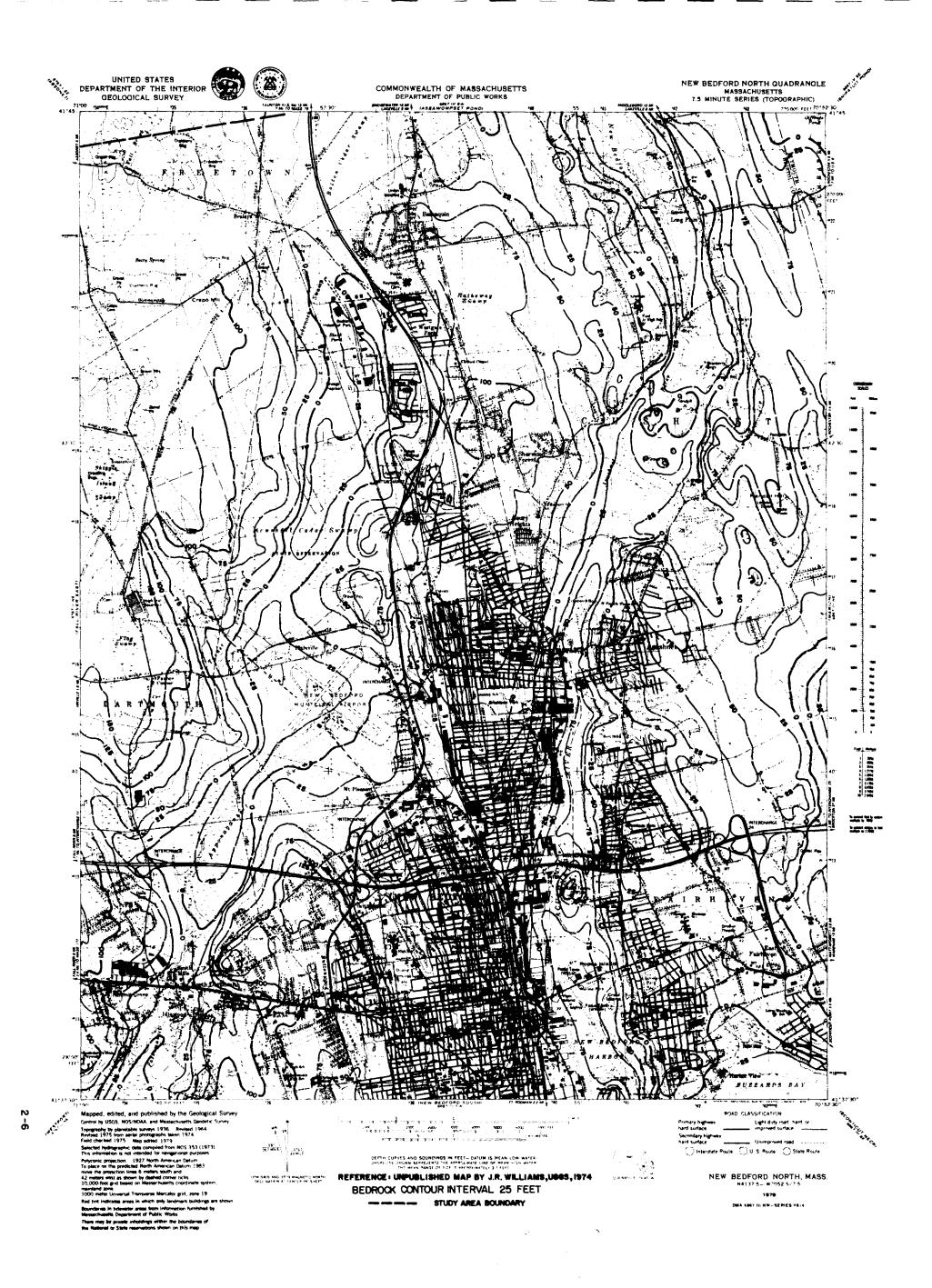
FALL RIVER EAST QUADRANGLE

HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I"= 4000"





APPROXIMATE BEDROCK SURFACE ELEVATIONS

NEW BEDFORD NORTH QUADRANGLE

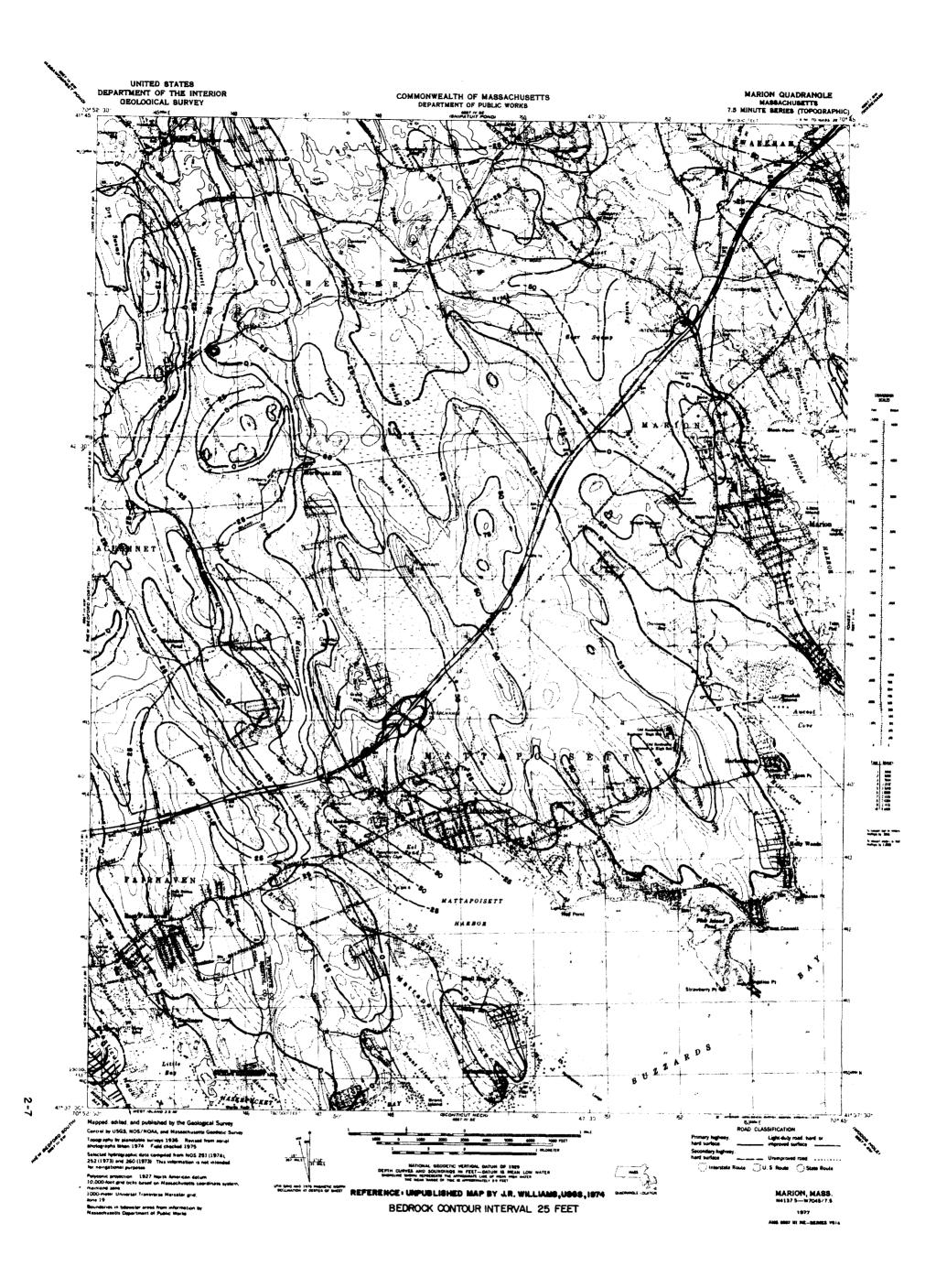
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

FIGURE 2-2D

COPPORATION

A Halliburton Company



APPROXIMATE BEDROCK SURFACE ELEVATIONS

MARION QUADRANGLE

HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

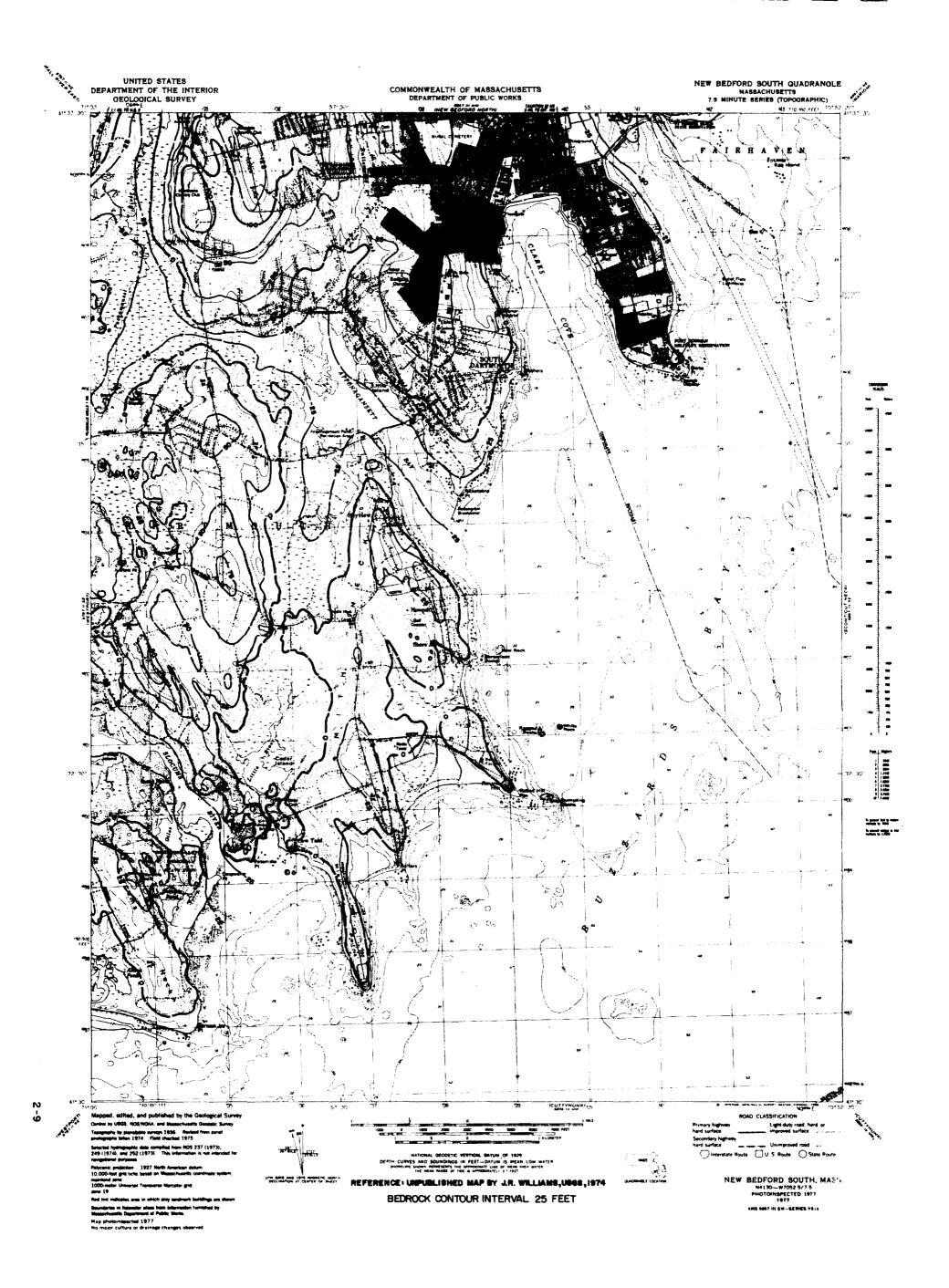
SCALE I"= 4000"





SCALE |"= 4000"





APPROXIMATE BEDROCK SURFACE ELEVATIONS

NEW BEDFORD SOUTH QUADRANGLE

HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE 1"= 4000



APPROXIMATE BEDROCK SURFACE ELEVATIONS
SCONTICUT NECK QUADRANGLE
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I" = 4000'



The bedrock configuration, in large part, determines the thickness of the overlying unconsolidated deposits. A greater thickness of material will be deposited in bedrock depressions. The saturated thickness of the unconsolidated material is, in turn, an important factor in determining the yield of an aquifer, along with other properties such as hydraulic conductivity.

Generalized maps of the surficial geology in the study area, developed from the work of Williams and Tasker (1978), are shown in Figures 2–3A through 2–3H. As seen in the figures, several types of unconsolidated materials are present, including peat, clay, silt, sand, gravel, boulders, and till. The types of material mapped together, singularly or in combination, differ by the size, sorting, water-bearing characteristics, and topographic expression. In addition, the deposits differ in surface runoff and infiltration capacities. Each mapping unit of unconsolidated material is described in greater detail in the following text.

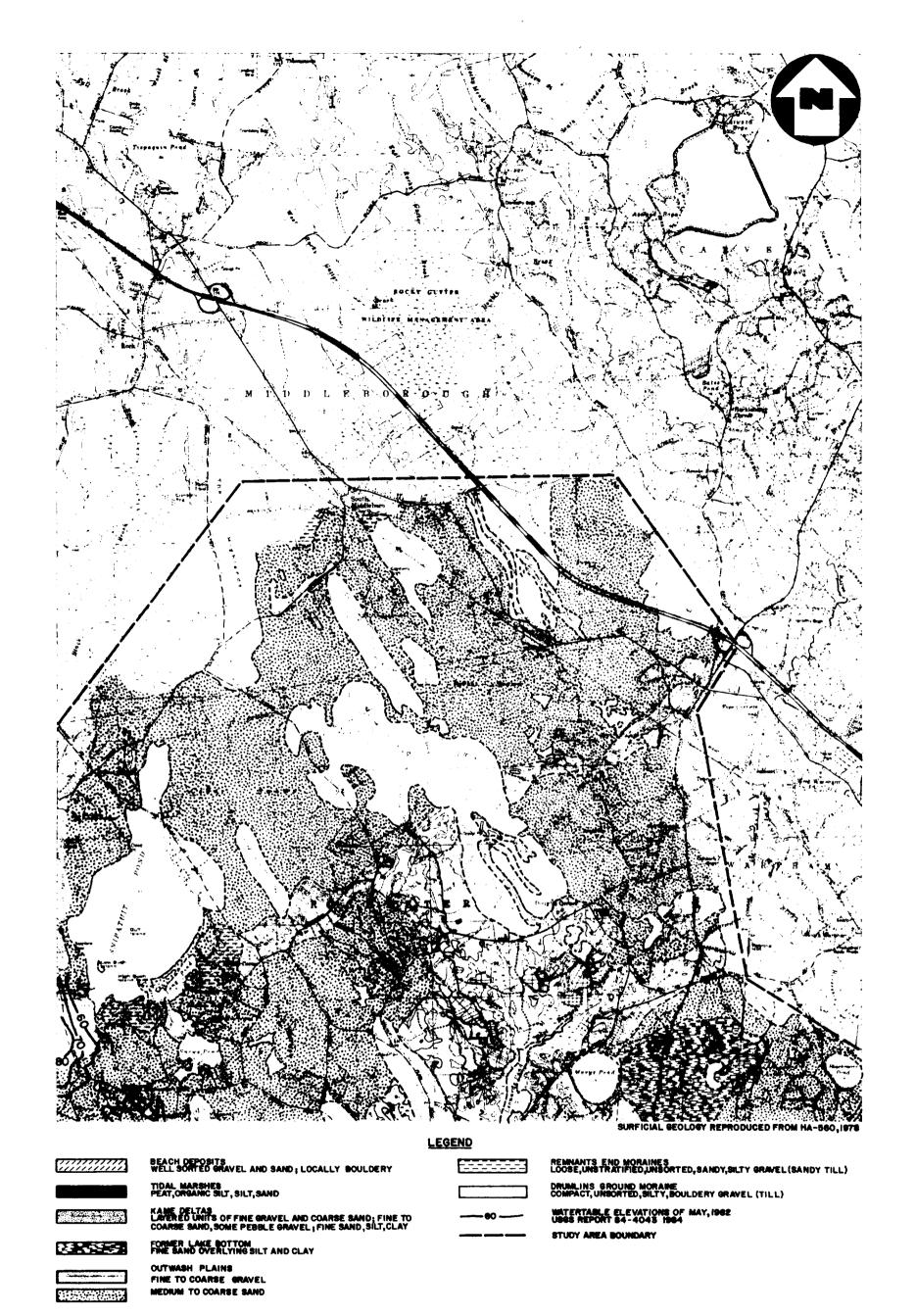
Glacial till comprises the greatest extent of surficial deposit within the study area. It lies immediately above bedrock in most areas and may be covered by other deposits. Till is composed of heterogeneous, unsorted sediments deposited by glacial ice with relatively no influence of meltwater. Two types of till have been described in New England, a basal till and an ablation till (Geoscience, 1980). Both have been identified in at least part of the study area (Dartmouth). The former type was deposited under moving ice and is compact, dense, and contains mostly silt and sand-sized particles. Ablation till was deposited as ice receded and is therefore generally loose, sandy, and contains few silt and clay particles. In the study area, the basal till forms the smooth-sloped drumlins and low-rolling, boulder-strewn ground moraine. The loose, unstratified sand ablation till forms the remains of glacial end moraines and occurs generally on hills and rarely in valleys.

Glacial end moraine remnants are scattered throughout the study area. They have been mapped south and southwest of Snipatuit Pond (Figures 2-3A and 2-3B), south of the Bolton Cedar Swamp in Acushnet (Figure 2-3D), and to the north of North Watuppa Pond (Figure 2-3C).



SURFICIAL GEOLOGY OF STUDY AREA
HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES
ASSAWOMPSET POND QUADRANGLE
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA
SCALE I"= 4000'





SURFICIAL GEOLOGY OF STUDY AREA
HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES
SNIPATUIT POND QUADRANGLE
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

FIGURE 2-3B

CORPORATION

A Halliburton Company



SURFICIAL GEOLOGY OF STUDY AREA

HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES

FALL RIVER EAST QUADRANGLE

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I"= 4000'

MEDIUM TO COARSE SAND





SURFICIAL GEOLOGY OF STUDY AREA

HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES

NEW BEDFORD NORTH QUADRANGLE

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

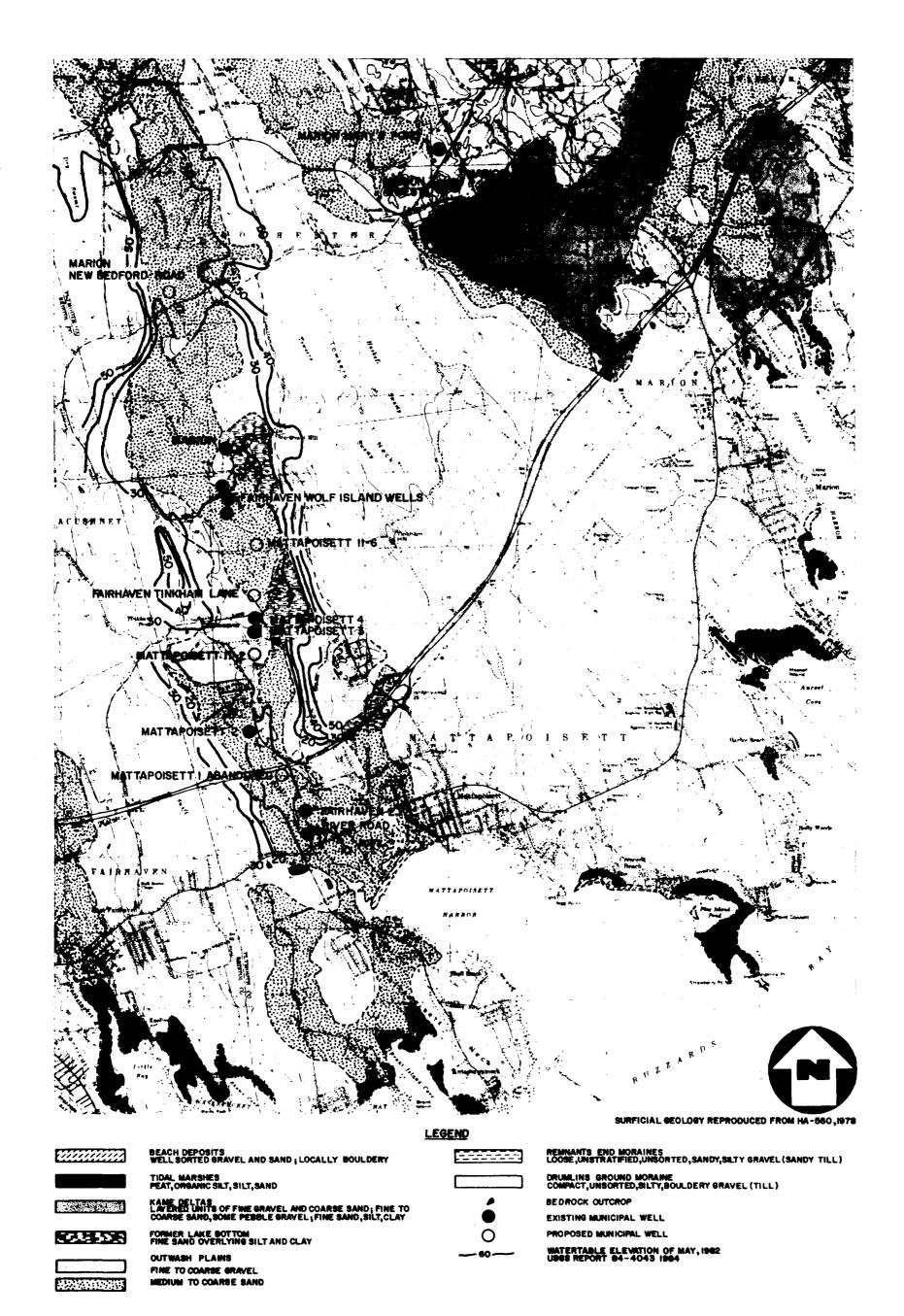
SCALE I" = 4000'

W BEDFORD, MA

COPPORATION

A Halliburton Company

FIGURE 2-3D



SURFICIAL GEOLOGY OF STUDY AREA
HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES

MARION QUADRANGLE

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I "= 4000"



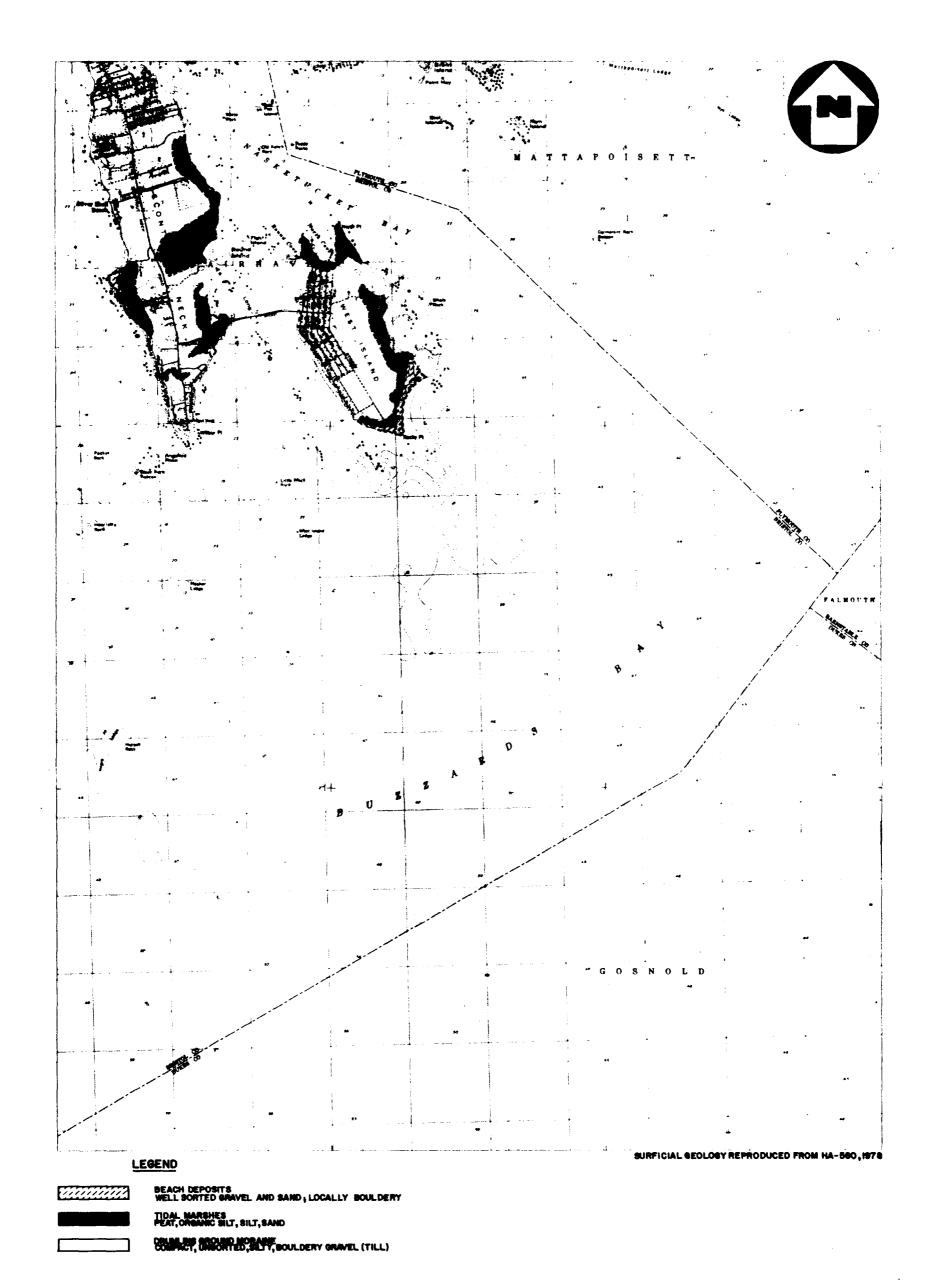


LEGENO BEACH DEPOSITS
WELL SORTED GRAVEL AND SAND; LOCALLY BOULDERY REMNANTS END MORAINES LOOSE, UNSTRATIFIED, UNSORTED, SANDY, SILTY GRAVEL (SANDY TILL) TIDAL MARSHES PEAT, ORGANIC SILT, SILT, SAND DRUMLINS GROUND MORAINE COMPACT, UNSORTED, SILTY, SOULDERY GRAVEL (TILL) KAME DELTAS LAYERED UNITS OF FINE GRAVEL AND COARSE SAND, FINE TO COARSE SAND, SOME PEBBLE GRAVEL, FINE SAND, SILT, CLAY BEDROCK OUTCROP EXISTING MUNICIPAL WELL FORMER LAKE BOTTOM FINE SAND OVENLYING SILT AND CLAY 0 PROPOSED MUNICIPAL WELL AVERAGE WATERTABLE ELEVATIONS GEOGGIENCE, 1990 ~~40~Z FINE TO COARSE GRAVEL MEDIUM TO COARSE SAND

SURFICIAL GEOLOGY OF STUDY AREA
HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES
NEW BEDFORD SOUTH QUADRANGLE
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I"= 4000'





SURFICIAL GEOLOGY OF STUDY AREA

HYDROGEOLOGIC INVENTORY OF GROUNDWATER RESOURCES

SCONTICUT NECK QUADRANGLE

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

FIGURE 2-3H

COPPORATION

A Halliburton Company

The remainder of the unconsolidated glacial materials mapped in the study area were deposited and stratified by meltwater and are generally termed outwash. The fine to coarse gravel and medium to coarse sand form the southward sloping outwash plains and local areas of pitted kames. Kames are low mounds or knobs composed of stratified sand and gravel deposited by a subglacial stream as a fan or delta at the margin of a melting glacier. Kame deltas also formed in temporary glacial lakes. These deposits consist of an upper 15 to 20 feet of well-sorted fine gravel and medium to coarse sand. A middle unit is composed of fine to coarse sand and some pebble gravel, and a lower unit, of fine sand, silt, and clay of variable thickness. The kame deposits generally rest on till.

Outwash deposits are found in lowlands and stream valleys, covering buried bedrock valleys. Within the study area, the outwash plains contain more gravel in the west than in the east; and grade to finer materials southward. Large expanses of outwash plains are prevalent in the study area. The largest area covered by these deposits is located in the northwest corner of the study area. This sand and gravel plain extends, almost uninterrupted, across the towns of Rochester and northern Marion (Figures 2–3B and 2–3E). Another outwash plain extends from a portion of Freetown into northern Acushnet (Figures 2–3A and 2–3D). The lowlands of Dartmouth are also underlain by sand and gravel outwash (Figures 2–3C, 2–3D, 2–3F, and 2–3G). Extensive glacio-fluvial deposits occur in the Mattapoisett, Acushnet, Paskamanset, and Slocums River valleys (Figures 2–3D, 2–3E, 2–3F, and 2–3G).

Sand, silt, and clay have also been deposited as remnants of former glacial lake bottoms. These lake bottoms generally consist of silt and clay deposits totaling 10 to 50 feet thick. The finer lake-bottom particles occasionally lie above stratified sand and gravel but generally lie on compacted till. Former glacial lake bottom deposits occur in several areas. However, they are of much smaller areal extent than the outwash plains. One deposit occurs to the east of Mary's Pond in the town of Marion (Figure 2-3B). Three small areas of these deposits occur in the Mattapoisett River Valley and in the town of Acushnet (Figures 2-3D and 2-3E).

Larger expanses of lake-bottom deposits underlie the Acushnet Cedar Swamp and the Apponaganset Swamp and occur to the east of South Watuppa Pond (Figures 2-3C and 2-3D).

Tidal peat occurs on flat tidal marshes, which are flooded during high tide. The peat is generally underlain by organic silt, silt, and fine to medium sand. The thickness of these units usually totals less than 30 feet. The tidal peat group generally overlies silt, sand, gravel, and compact, silty gravel. Tidal peat areas generally ring the harbors and coves within the study area. For instance, they can be found along the shores of Sippican Harbor, Aucoot and Hiller Coves, Mattapoisett Harbor, and Nasketucket Bay (Figures 2–3E, 2–3F, 2–3G, and 2–3H).

The last major type of unconsolidated material present in the study area is the beach deposits, which may be as much as 30 feet thick. They consist of well-sorted gravel and fine to coarse sand, with boulders in some locals. The deposits generally overlie stratified silt, sand, gravel, tidal-marsh organic deposits, or till. These deposits are located on the bay shorelines, such as at West Island and Horseneck Beach (Figures 2-3F, 2-3G, and 2-3H).

3.0 OCCURRENCE OF GROUNDWATER

3.1 General Principles

Groundwater occurs under unconfined or confined conditions in the unconsolidated materials and in the underlying bedrock. Under unconfined conditions, precipitation and recharge enter the groundwater reservoir by downward percolation. The upper surface of the saturated zone, which is under atmospheric condition, is called the water table. The static water level in wells screened in an unconsolidated zone generally designates the position of the watertable.

Unconfined groundwater flows from areas of higher water-table elevations (higher potential energy) to areas of lower water-table elevations (lower potential energy). Simply stated, groundwater from the higher topographic area flows through the stratified glacial drift and discharges primarily to streams, ponds, and wetlands, which occupy the low-lying, lower head areas. However, during dry periods when water levels have declined, surface water bodies, such as streams, recharge the underlying aquifers through permeable bottoms. In addition, pumping from the unconsolidated aquifer can alter patterns and/or induce infiltration from the streams into the aquifer. Thus, groundwater and surface water flow are hydraulically connected.

In Massachusetts, the annual cyclic rise and fall of the water table in areas not affected by pumping results from seasonal differences in the rate of groundwater recharge and the relatively constant discharge (Frimpter, 1981). Maximum groundwater recharge occurs during late winter or early spring, usually in March and April, as a result of precipitation and snowmelt. The water levels are lowest during late spring and early fall because of high evapotranspiration. The aquifers discharge groundwater through springs or by seepage into streams, by evapotranspiration and by pumping from wells.

Groundwater in the confined condition occurs when water moving through an aquifer passes beneath a relatively impervious rock or stratum (called an aquitard or aquiclude) and becomes confined under pressure. Recharge enters laterally into

the confined zone or vertically by leakage through the confining layer. The water level in wells penetrating a confined aquifer will be found above the bottom of the confining layer. Confined aquifers are also known as artesian aquifers.

Porosity, hydraulic conductivity, and transmissivity values of the deposits are important parameters in determining the occurrence and movement of groundwater. Porosity is a measure of the amount of void space within individual particles in a deposit and thus indicates the amount of area available to store water. Hydraulic conductivity is the ability of the soil or rock medium to transmit water from storage. The transmissivity equals the product of the hydraulic conductivity and the saturated thickness of the deposit. The size, packing, and sorting of particles affects the porosity and hydraulic conductivity. Even though a deposit may have a large percentage of voids, the arrangement of the particles may preclude significant groundwater movement; such a situation exists in clay deposits. Williams and Tasker (1978) have determined general hydraulic conductivity values for each type of deposit discussed above. Table 3-1 presents these measurements in feet per day (ft/day).

Even though some water can be found in most unconsolidated deposits and in the bedrock, locating significant, reliable groundwater resources in glaciated regions is difficult and can best be accomplished by a combination of mapping, geophysical exploration, and test drilling. Repeated glacial events have altered and obscured the bedrock. The glaciers and their meltwaters have rearranged drainage patterns, deposited new material, and modified and created new landforms. In many cases the surface provides no evidence that favorable groundwater resources are concealed beneath. Exploration difficulties can be lessened by knowing general water-bearing characteristics of each type of deposit and their topographic positions. Therefore, favorable groundwater reservoirs can be delineated before detailed field explorations are undertaken.

TABLE 3-1
ESTIMATED HYDRAULIC CONDUCTIVITY OF DEPOSITS IN STUDY AREA

Type of	Lithology	Hydraulic Conductivity (feet/day)
Beach	Well Sorted Gravel	150
	Fine to Coarse Sand	40-150
Tidal	Tidal Peat, Organic Silt, Silt	10
	Fine to Medium Sand	40-100
Kame Delta	Well Sorted, Fine Gravel	150-200
	Medium to Coarse Sand	100-150
	Fine to Coarse Sand	40-150
	Pebble Gravel	150-200
	Fine Sand	40
	Silt and Clay	10
Lake Bottom	Fine Sand	40
	Silt and Clay	10
Outwash Plains	Fine to Coarse Gravel	150-475
	Medium to Coarse Sand	100-150
Glacial End	Loose, Sandy Till	100
Moraines	Sandy, Bouldery Gravel with Stratified Sandy Gravel	250
Drumlins and Ground Moraines	Compact, Silty, Bouldery Till	10

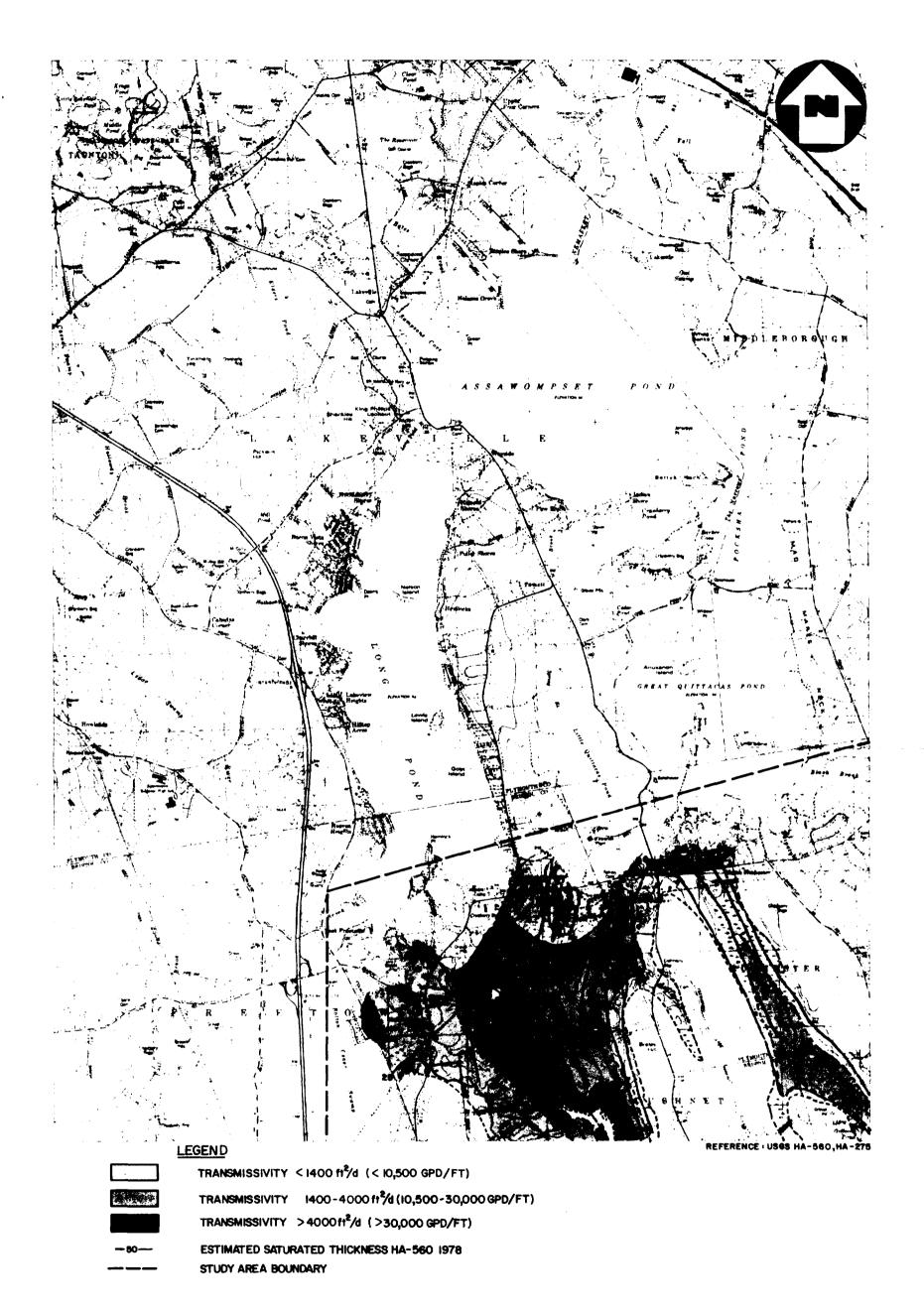
3.2 Occurrence of Groundwater in Unconsolidated Deposits

General water-bearing characteristics of the unconsolidated materials present in the study area are discussed in this section. Figures 3-1A through 3-1G present estimated transmissivities of the unconsolidated deposits in the study area, as well as the saturated thicknesses of the aquifers. More specific information on Mattapoisett River area deposits is also presented.

The USGS Water Resources Division conducted a groundwater modeling study of the Mattapoisett River Aquifer and published the results in a report by Olimpio and deLima in 1984. The model was used to determine the long-term impacts of increased groundwater withdrawals on groundwater levels and streamflow. The report contained information on aquifer characteristics, groundwater flow, water quality, and municipal water systems. Although the report included data on just the Mattapoisett River Aquifer, it is likely that similar aquifer characteristics, groundwater regimes, and water resource concerns occur throughout the study area.

Williams and Tasker (1978) indicate that the elevation of the water-table varies with topography and type of deposit. Depth to water is greatest on summits and upper slopes and closer to the surface in depressions and near the base of drumlins. The overlying silt, sand, and gravel are generally unsaturated. In general, it has been found that eskers, kames, and kame terraces are commonly found in topographic positions well above adjacent streams. Drainage in these features is usually effective, and few saturated zones are found within the ice contact deposits.

Till can sometimes supply enough water for domestic purposes. Water is usually obtained from shallow dug wells, which are finished in underlying bedrock or the overlying till deposits. The thickness of the till deposits and the characteristics of the till within the study area have not been determined to a large extent. Tills have large lateral and vertical variations in composition and hydraulic conductivity. Therefore, the ability to transmit water varies horizontally and vertically.



APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

ASSAWOMPSET POND QUADRANGLE

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE 1"= 4000'





APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES
SNIPATUIT POND QUADRANGLE
NEW REDECRD HARROR STUDY NEW REDECRD MA

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA SCALE I" = 4000' FIGURE 3-1B

FIGURE 3-1B

CORPORATION

A Halliburton Company

APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES
FALL RIVER EAST QUADRANGLE

TRANSMISSIVITY 1400-4000 ft²/d (10,500-30,000 GPD/FT)

TRANSMISSIVITY > 4000ft2/d (> 30,000 GPD/FT)

SATURATED THICKNESS GEOSCIENCE, JULY, 1980 STUDY AREA BOUNDARY EXISTING MUNICIPAL WELL

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA SCALE I"= 4000" FIGURE 3-1C

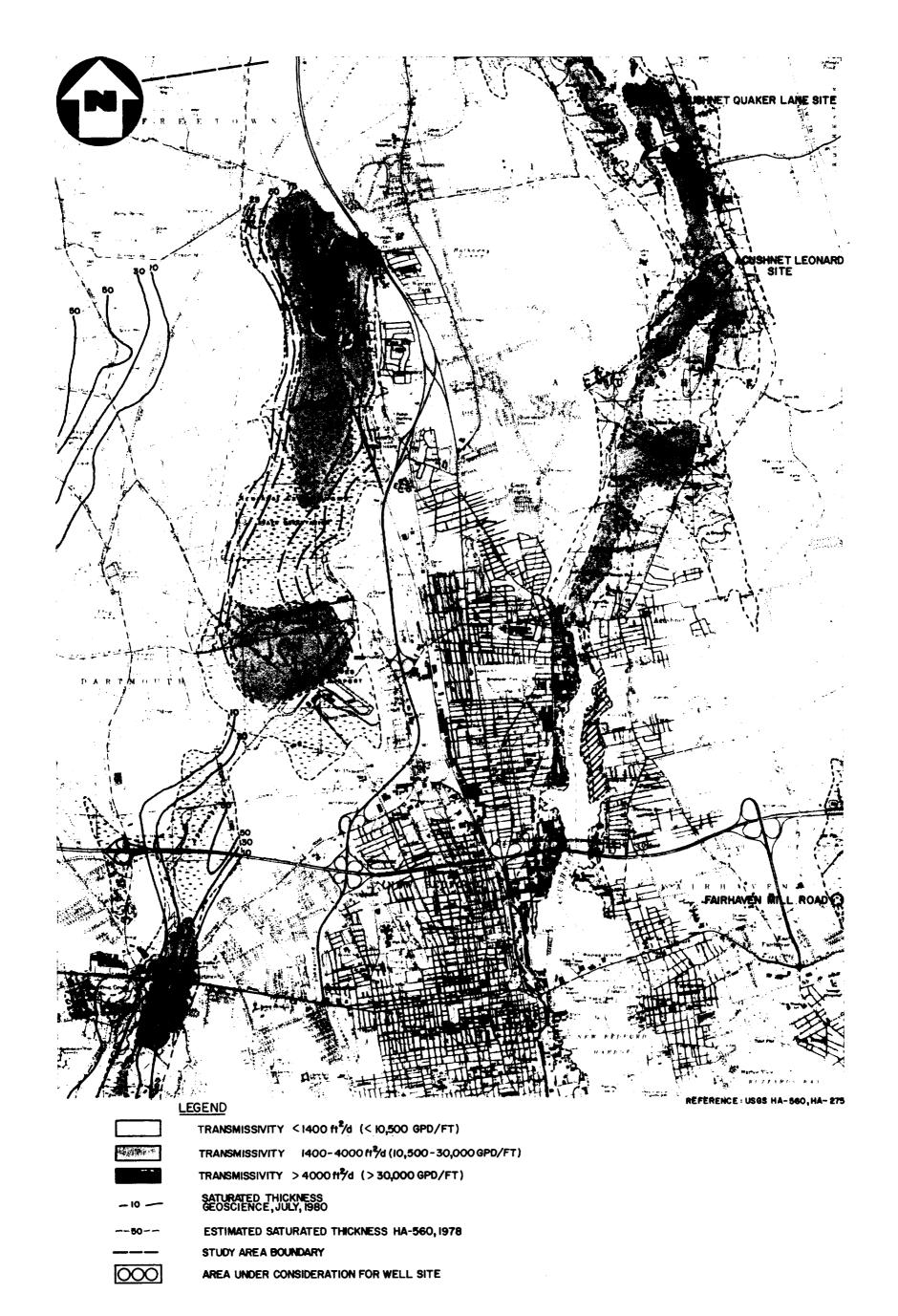
FIGURE 3-1C

COPPORATION

A Halliburton Company

3-7

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APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES

NEW BEDFORD NORTH QUADRANGLE

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I"= 4000"



APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES MARION QUADRANGLE

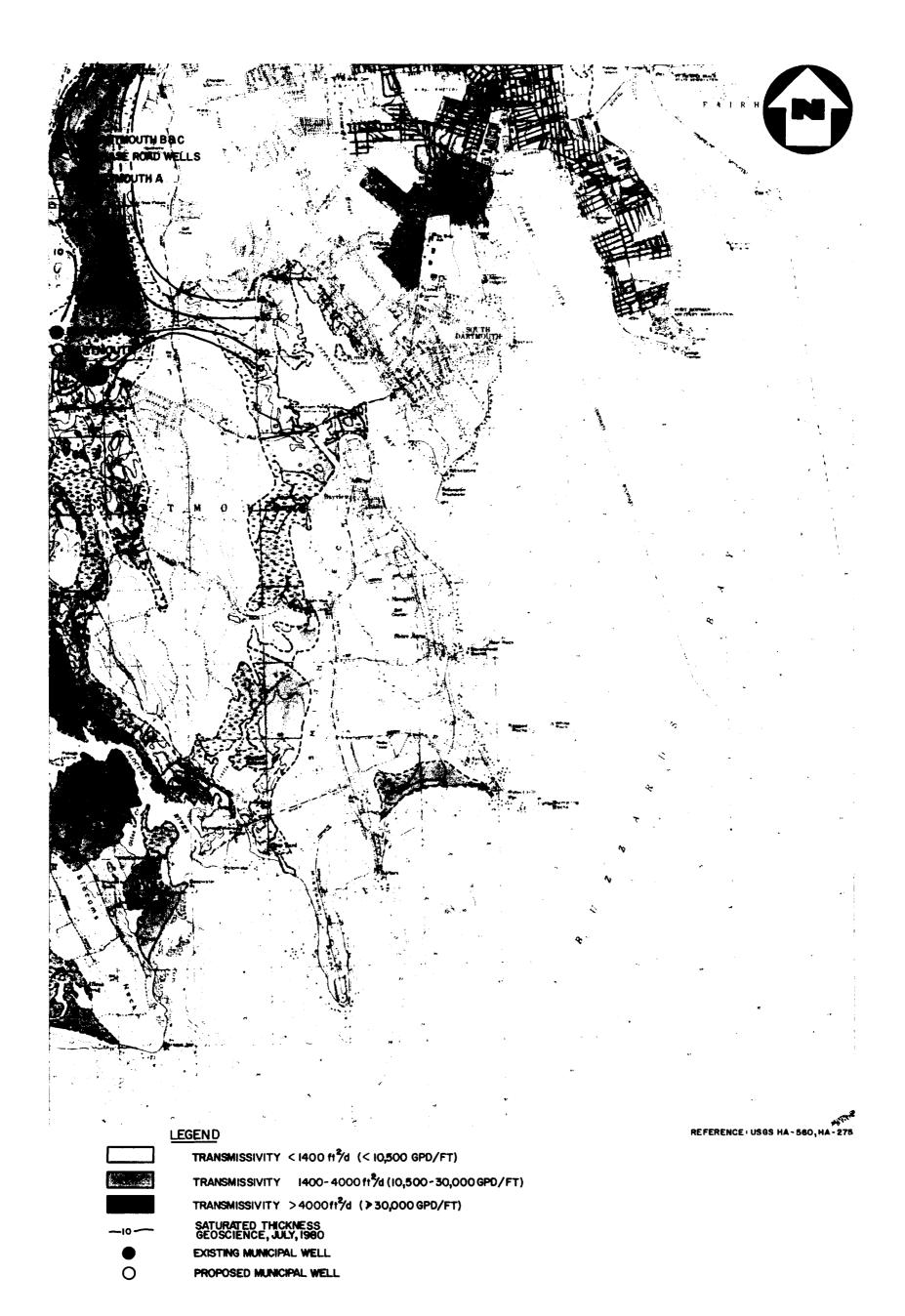
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA SCALE I"= 4000'





APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES
WESTPORT QUADRANGLE
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA
SCALE I"= 4000'





APPROXIMATE TRANSMISSIVITIES OF UNCONSOLIDATED DEPOSITS
HYDROGEOLOGIC INVENTORY OF GROUND WATER RESOURCES
NEW BEDFORD SOUTH QUADRANGLE
NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE I"= 4000'



Groundwater velocity in till is generally much slower than in the coarser grained, stratified material. If the till is relatively impermeable, a perched water table may occur or the till may serve as a confining layer or leaky aquifer to an underlying aquifer. However, the rate of vertical and horizontal movement can be significantly greater when the till is sandy, bouldery, or contains coarse-grained lenses. Groundwater from the till may leak into the outwash, as discovered by the USGS during a study conducted in the Mattapoisett River Aquifer.

The water-level within the fine sand, silt, and clay of former lake bottoms is generally within 10 feet of the land surface. The surficial sand deposits have a moderate infiltration capacity and little surface runoff. Large supplies of water are limited to local deposits of the underlying sand and gravel. Figure 2-3E shows the location of a Marion municipal well bordering a former lake-bottom deposit.

Infiltration capacity is poor in the tidal deposits, and the water-table is closer to the surface. Dissolved solids concentrations in the water are usually greater than 500 milligrams per liter (mg/l) because of the intrusion of seawater. Transmissivities in these deposits are usually less than 10,500 gallons per day per foot (gpd/ft). However, at the Dartmouth Violetta Site and the Marion main well field, the transmissivities are greater than 30,000 gpd/ft.

The well-sorted gravel and fine to coarse sand of the beach deposits have little surface runoff and high infiltration capacities. Water within beach deposits also has a high dissolved solids content, and chances of finding large quantities of fresh water are poor. The water table is generally within 10 feet of the surface. Transmissivities are in the same range as the values for tidal deposits.

The largely unconfined stratified sand and gravel beds of the glacial outwash deposits, which fill the valleys, are the principal water supply sources. They are generally an excellent source of large supplies of water in areas having more than 50 feet of saturated thickness. Commonly, these aquifers are connected with surface-water bodies, and wells pumping from glacial outwash deposits can induce surface water to infiltrate through permeable stream- and lake-bottom sediments into the aquifer.

The relief and configuration of the bedrock surface determines, to a great extent, the thickness of overburden and the amount of water potentially stored in the overburden. Thus, preglacial buried valleys are the locations of the thickest deposits of saturated material (Geoscience, 1980). As seen in Figures 2-3A through 2-3H, the majority of the municipal well fields within the study area and are located in the gravel and sand outwash deposits. Figures 3-1A through 3-1G show the estimated saturated thickness of the aquifers at the well locations. These locations were presumably chosen because the aquifers had the following characteristics:

- Sufficient porosity and hydraulic conductivity
- Sufficient saturated thickness
- Sufficient recharge area
- Acceptable water quality (Geoscience, 1980)

Table 3-2 presents estimated aquifer characteristics for the municipal well sites. The data was compiled from results of actual pumping tests or published and unpublished USGS reports.

3.3 Occurrence of Groundwater in Bedrock

Bedrock aquifers are recharged by leakage from the overlying unconsolidated aquifers. The upper weathered zones in bedrock, joints, and fractures store water and allow the water to continue to move downward through the crystalline rock. Therefore, the immediate source of water to deeply drilled bedrock wells is joints and faults, but these openings conducted water originally stored within the overburden.

The percentage of pore space within crystalline rocks is small compared to the porosity of the overburden, especially in sand and gravel. Unweathered metamorphic and igneous rocks have primary porosities less than 3 percent. However, increased porosities and hydraulic conductivities are developed through fracturing and weathering (Davis, DeWiest, 1966). The average hydraulic

TABLE 3-2
ESTIMATED AQUIFER CHARACTERISTICS
MUNICIPAL WELL SITES

Well	Lithology	Saturated Thickness (ft)	Hydr <u>Condu</u> apd/ft ²		Transn apd/ft	nissivity ft ^Z /day	Pumping Rate (MGD)	Capacity (MGD)	Remarks
*Dartmouth Rt. 6	Fine to coarse gravel	36	1,830	245	66,000	8,844	-	0.45	Closed
*Dartmouth Violetta	Fine gravel, medium to coarse sand	50	1,510	202	75,500	10,141	-	0.465	
*Dartmouth Chase Rd. A	Fine to coarse gravel	37	1,220	163	45,000	6,022	-	0.465	Gravel packed
*Dartmouth Chase Rd. B & C	Fine to coarse gravel	37	1,430	192	52,800	7,075	-	0.500	Gravel packed
**Dartmouth proposed	Fine to coarse gravel	30	1,125	150	33,750	4,500	-	0.5	-
**Dartmouth (N. Russell Mill Rd.)	Fine to coarse gravel	25	1,125	150	28,125	3,750	-	-	-
**Acushnet proposed Quaker Lane Site	Fine gravel and medium to coarse sand	30	1,125	150	33,750	4,500	-	-	Need chlorine treat- ment
**Acushnet proposed Leonard Site	Fine to coarse gravel	30	1,125	150	33,750	4,500	-	0.8	Need chlorine treat- ment
**Marion (main well)	Sand overlying silt,	25	>1,200	>160	>30,000	>4,000	-	0.3	Thirty 2-1/2 inch wells

3-14

TABLE 3-2
ESTIMATED AQUIFER CHARACTERISTICS
MUNICIPAL WELL SITES
PAGE TWO

Well	Lithology	Saturated Thickness (ft)	Hydra Conduc gpd/ft ²		Trensm gpd/ft	issivity ft ² /day	Pumping Rate (MGD)	Capacity (MGD)	Remarks
**Marion (Mary's Pond)	Fine to coarse gravel	50	>600	>80	>30,000	>4,000	-	0.34	Twenty-five 2-1/2 inch wells
**Marion - east	Fine to coarse gravel	50	>600	>80	>30,000	>4,000	-	Combined east and west 0.5	Gravel pack
**Marion - west	Fine to coarse gravel	50	>600	>80	>30,000	>4,000	-	Combined east and west 0.5	Gravel pack
eseMarion (New Bedford Rd.) proposed	Medium to coarse sand	60	1,200	160	72,000	9,600	-	0.8	-
***Merion (North Wolf Island Rd.)	Fine to coarse gravel	59	1,463	195	87,000	11,505	0.35	8.0	Gravel pack
***Fairhaven Wells (Wolf Island Rd.)	Medium to coarse gravel	59-68	308-683	41-91	18,000- 46,500	2,419- 6,188	-	0.76	Confined aquifer
***Fairhaven 2 River Road	Medium to coerse send	25	420-1, 20 0	56-160	10, 500 - 30,000	1,400- 4,000	0.37	0.72	40 tubular wells
**Fairhaven Tinkham Lane	Sand and gravel	50	>600	>80	>30,000	>4,000	-	-	-

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TABLE 3-2 **ESTIMATED AQUIFER CHARACTERISTICS** MUNICIPAL WELL SITES PAGE THREE

		Saturated Thickness	Hydra Condu		Transm	nissibility	Rate	Pumping Capacity	
Well	Lithology	<u>(ft)</u>	apd/ft ²	ft/day	gpd/ft	ft ² /day	(MGD)	(MGD)	Remerks
**Fairhaven Mill Rd.	Medium to coarse sand	25	750- 1,125	100-150	18,750- 28,125	2,500- 3,750	-	0.7	30 tubular wells may dry up
***Mattapoisett 11-6 proposed	Medium to coarse sand	70	1,125	150	78,750	10,500	~	0.50	Three 8-inch test wells
***Mattapoisett 4	Fine to coarse gravel	63	1,500	200	94,500	12,600	0.34	1.00	Gravel pack
***Mattapoisett 3	Fine to coarse gravel	60	1,275	170	76,500	10,200	0.10	0.80	Gravel pack
**Mattapoisett 11-2 proposed	Fine to coarse gravel	40	260-750	35-160	10,500- 30,000	1,400- 4,000	•	-	2-1/2 inch test well
***Mettapoisett 2	Medium to coarse sand	25	420-1,200	56 - 160	10,500- 30,000	1,400 4,000	0.01	0.15	Oriven 2-1/2 inch wells
**Mattapoisett 1 Abandoned	Medium to coarse sand	25	<420	<56	<10,500	<1,400	~	-	-

Figures compiled from Geoscience report, "Dartmouth Groundwater Resource Study," July 1980.

^{**} Figures estimated from USGS Hydrologic Atlas HA-560.
*** Figures taken form USGS Water Resources Report 84-4043.

conductivity decreases with depth, since surface disturbances tend to penetrate only a short depth. The joints, faults, and fractures will usually dissipate with depth.

Wells located in igneous and metamorphic rock may yield enough water for domestic supplies. The difference in well yields usually reflects differences in the degree of weathering (for shallow bedrock wells) or of fracturing rather than variations of mineralogy or rock fabric. The favorable water-bearing areas are weathered zones and extensive fracture zones associated with fault zones that have not been recemented (Davis, DeWiest, 1966). Thus, the frequency of fracturing and the interconnection of the fractures is critical in developing a significant bedrock water supply. Since the occurrence, extent, and interconnection of joints and fractures may be highly variable within even short distances, obtaining a significant, reliable supply of groundwater can be difficult.

The Massachusetts Water Resources Commission retains driller logs of domestic wells, many of which obtain water from the bedrock. The ranges of depth to bedrock, water level, and initial groundwater yield of selected domestic wells from each of four municipalities within the study area are listed below:

Municipality	Range of Depth to Bedrock	Range of Depth to Water Table	Range of Initial Yield
Acushnet	14-129'	3-30′	0.5-205 gpm
Dartmouth	30-105'	16.5-27'	4 gpm
Mattapoisett	20-30′	8-25'	3-15 gpm
Rochester	47-75'	9-28'	0.75-168 gpm

Comparing the depth of the wells and the elevation of the water table, it is apparent that these selected wells do not obtain their water from bedrock aquifers. Borehole lengths in some circumstances may be extended to bedrock to provide enough storage volume for the well, however.

3.4 Groundwater Movement and Pumping Effects

Groundwater flow velocity is dependent on several factors: the slope (or gradient) of the water table, the hydraulic conductivity, the porosity of the deposit, and the boundary conditions. These factors may change if there are vertical and/or horizontal variations within the deposit. According to Freeze and Cherry (1979), the hydraulic conductivity is also dependent on the position within the aquifer and thus can vary in the direction of measurement. This property, referred to as "trending heterogeneity," is particularly common in response to sedimentation processes such as that which deposits glacial outwash.

Pumping tests supervised by Fay, Spofford & Thorndike for the town of Dartmouth show such a directional change in hydraulic conductivity. In this instance, the Dartmouth, 24-inch-diameter, gravel pack well located about 1,000 feet east of Chase Road and 2,500 feet north of Russells Mills Road (Figure 2-3G) was pumped for 17 days at three different pumping rates. Drawdown readings were taken in six observation wells, which were located radially at varying distances around the pumping well. The average hydraulic conductivity of the deposit was approximately an order of magnitude higher (approximately 17,000 gpd/ft²) when measured in the north-south direction than in the east-west direction (approximately 2,500 gpd/ft²). This preferred flow direction probably reflects the direction in which the materials were originally carried and deposited by meltwaters, and thus contains a higher degree of alignment.

In the USGS study of the Mattapoisett River Aquifer (Olimpia, deLima, 1984), the movement of the groundwater and effects of pumping also were explored to a greater degree than elsewhere in the study area. The findings of this study are valuable for predicting groundwater flow patterns elsewhere in deposits of similar hydrogeologic characteristics. The effects of pumping in the Mattapoisett River Aquifer and well interferences were also discussed. These situations may occur in other locations of the study area where concentrated pumping occurs.

As seen on Figure 2-3E, the Mattapoisett River Aquifer is approximately 8 miles long and 1 mile wide, located mostly in Rochester and Mattapoisett. Till deposits

form the uplands on the east and west sides of the valley and in the center of the valley underlying the drift. The stratified drift deposits form the lowlands of the river valley and range from a few feet thick near aquifer boundaries to more than 100 feet thick in the center of the valley at the Fairhaven well site. In most locations, the drift ranges from 30 to 70 feet thick (Olimpio, deLima, 1984). The bedrock is generally flat except for the deep channel in the center of the valley. The boundary between the till and the drift has a downward slope toward the center of the river.

The stratified drift comprises the main aquifer throughout the study area and consists mostly of fine to medium sand. The Mattapoisett River, which flows over the aquifer, is hydraulically connected to the aquifer responding both to drought and pumping stresses (Olimpio, deLima, 1984). The groundwater in the stratified drift aquifer is mostly unconfined, except beneath a silt-clay layer (see below) of limited areal extent. The stratified drift is recharged from precipitation and lateral leakage from the till. The aquifer discharges water to the river and to small ponds in the valley. Water is removed from this system by evapotranspiration and groundwater pumpage.

The aforementioned clay and silt layer interbedded in the stratified drift is located in the vicinity of Wolf Island Road (location of the Fairhaven Wolf Island Road wells, Figure 2–3E). It is 10 to 60 feet thick and separates an upper 10– to 20–foot–thick sand and gravel layer. From Wolf Island Road, the clay–silt layer extends northward approximately 1500 feet to a point just south of the Marion supply well. The clay–silt bed extends southward approximately 2,000 feet to the vicinity of the Mattapoisett test well site 11–6. The eastern and western margins of the layer are not well defined; however, the available data indicates that the layer is about 2500 to 3000 feet wide and extends beneath portions of Branch Brook and the Mattapoisett River (Olimpio, deLima, 1984).

Water from the recharge areas in the Mattapoisett River basin flows through the stratified drift and discharges primarily to the river and its tributaries. Water table contours on Figure 2-3E show the movement of water from the higher elevations of the adjacent till plains toward the stratified drift in the center of the

valley. The elevation of the water table ranges from near sea level at the coast to nearly 90 feet in the northern part of the valley. Olimpio and deLima indicate that vertical flow may occur along the till/stratified drift boundary, within and adjacent to the silt-clay layer at Wolf Island Road, in the immediate vicinity of pumping wells, and beneath the streambed of the Mattapoisett River.

All of the municipal wells in the Mattapoisett River valley are located within a hundred feet of the river or its tributary, Branch Brook. Details on the pumping rates of the wells are included in the next section. Except for the three Fairhaven wells, these municipal wells are completed in the unconfined drift aquifer and are hydraulically connected with the river. The Fairhaven wells are completed through the clay-silt layer into the confined sand and gravel aquifer. It does not appear that these wells are connected with Branch Brook or the river (Olimpio, deLima, 1984).

Several pumping tests were conducted the Mattapoisett River Aquifer, and observations were made in adjacent wells and the river. First, these tests confirmed that municipal pumpage from the aquifer induces infiltration from the river. Second, measurements showed a reduced streamflow downstream of the pumping municipal wells. Third, the high withdrawal rates from the relatively closely spaced wells in the vicinity of Wolf Island Road caused interference effects throughout the area. The interference from each pumping well affected the yield of the other wells.

The wells completed in the confined layer also interfered with the other Marion and Mattapoisett wells. Olimpio and deLima calculated that the total well interference at the Fairhaven site ranges from 15 to 25 percent of the saturated thickness of the stratified drift. In addition, the range of interference is equal to, and in some places greater than, the thickness of the confined aquifer in which the wells are finished. Olimpio and deLima concluded that the amount of well interference was controlled chiefly by the rate, duration, and timing of water withdrawals from each well.

Besides pumping stresses, the localized groundwater flow patterns may also be changed by artificial recharge areas created by man's activities, such as flooding an area for cranberry cultivation. One such cranberry operation is located in the vicinity of the Mattapoisett municipal wells, which yield a groundwater mounding effect (Figure 2–3E).

4.0 MAJOR WATER SUPPLIES

Figures 2-3C through 2-3G present the existing and proposed well locations and surface water sources used by municipalities in the study area. Information on existing water systems and well yields was obtained from municipalities, the USGS, engineering consultants reports, the Massachusetts DEQE, and the Massachusetts Water Resources Commission. As part of the Massachusetts River Basin Planning Program, the Commission sent out questionnaires to municipalities in December 1982 and received the responses in January 1983. The questionnaires covered such topics as the source and capacity of pubic water systems and any problems with water quality. Table 4-1 illustrates present and future water consumption figures and service population for each municipality. Specifics on each water supply are discussed by individual town below.

Several municipalities within the study area do not have public water systems. The vast majority of residents of the towns of Rochester, Westport, and Freetown rely on domestic wells. A small area of East Rochester, near the Wareham line, is serviced by the Wareham Fire District. In addition, Rochester residents along the route of Marion water mains receive water from Marion. A small population in Freetown receives water from New Bedford. Water quality problems discovered during monitoring for several muncipalities are identified in the Section 5.3.

4.1 Surface Water Supplies

Acushnet presently obtains 100 percent of its water from the New Bedford surface water supply. However, the town has conducted explorations for a possible groundwater supply. The two proposed locations are the Quaker Lane site, north of Lake Street, and the Leonard well site, south of Leonard Street (Figure 2-3D). Both sites are just to the west of North Main Street. The Massachusetts Board of Health approved the Leonard well site in 1966. Chlorine treatment would be required. The three test wells at the site have an estimated capacity of 0.8 million gallons per day (MGD).

TABLE 4-1
MUNICIPAL WATER SUPPLY STATISTICS

Muncipality	1980 Service Population	Water Source	Average Day Demand (MGD)	Maximum Day Demand (MGD)	1990 Estimated Service Population	1990 Projected Average Day Demand (MGD)	1990 Projected Maximum Day Demand (MGD)
Acushnet*	6,528 New Bedford	Surface,	0.4	0.6	8,732	0.54	0.81
Dartmouth**	22,000 New Bedford	Wells.	2.1	3.5	25,480	2.35	4.70
Fairhaven**	14,971	Wells	1.3	2.7	16,317	1.45	2.47
Fail River	100,239	Surface	15.3	21.4	100,933	15.44	21.62
Marion	3,893	Wells	0.5	0.8	4,505	0.60	0.98
Mattapoisett Seasonal	4,588 +2,212	Wells	0.4**	0.8**	-	-	-

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Muncipality	1980 Service Population	Water Source	Average Day Demand (MGD)	Maximum Day Demand (MGD)	1990 Estimated Service <u>Population</u>	1990 Projected Average Day Demand (MGD)	1990 Projected Maximum Day Demand (MGD)
New Bedford							
Total	121,387	Surface	18.6	31.8	122,137	18.69	31.96
New Bedford	98,478						
Acushnet	6,528						
Freetown	400						
Dartmouth	8,196						•
Fairhaven	7,785						
Freetown	400	Surface, New Bedford	0.03	0.03	512	0.033	0.038

the state of the s

MGD = million gallons per day

4-3

^{*} Currently derives 100% of its water from New Bedford

^{** 1981} delly consumption figures

The Fall River Water Department obtains its water from North Wattuppa Pond and the Copicut Reservior (Figure 2-3C). Water from the reservoir flows into the pond. A treatment plant, located at the pond, consists of sand filters, chlorine units, alum units, and charcoal filters. The Water Department also serves approximately 8000 people in North Tiverton, Rhode Island. Fall River also has a water connection to Somerset, Massachusetts, in case either community needs an emergency supply. The water yields for North Watuppa and Copicut Reservior Pond are 9.5 MGD and 6.5 MGD respectively. The water from Noaquochoke Lake is contaminated and needs treatment. It is no longer used as a public water supply. Fall River has also investigated other potential supplies. A preliminary engineering report estimated that 2.3 MGD could be obtained from Rattlesnake Brook and about 2.8 MGD could be obtained from Bread and Cheese Brook (Figure 2-3C). Water from both these brooks may have to be treated. A report written on South Watuppa Pond indicated that the pond could yield 12 MGD but that treatment would be required.

The New Bedford Water Department obtains and fully treats water from Little Quitticas Pond, Great Quitticas Pond, Long Pond, and Assawompsett Pond (Figures 2-3A and 2-3B). The latter pond is only used occasionally, since it belongs primarily to Fall River. The New Bedford Reservoir was formerly the main city supply, but now it is used as an industrial water supply only (4 MGD).

4.2 Groundwater Supplies

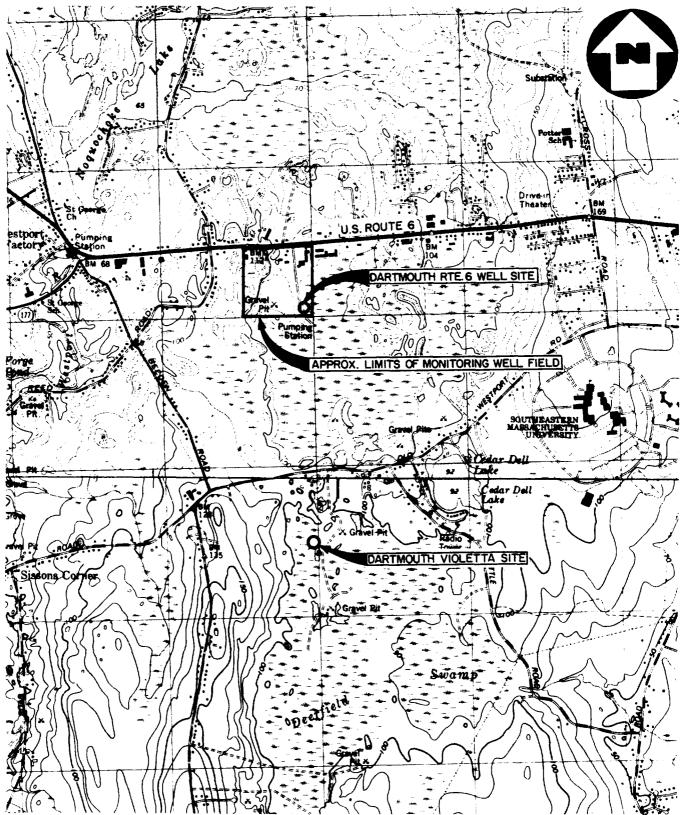
Dartmouth purchases approximately 44 percent of its water supply water from New Bedford. Water is pumped through two 48-inch mains from New Bedford's Quitticas station to the High Hill Reservoir in Dartmouth. Water flows by gravity from the reservoir into the city. The town obtains the rest of its supply from three groundwater sources: the Dartmouth A, B, and C well site (east of Chase Road); a new well just north of Russell Mill Road and east of Chase Road; and the Violetta well (Figures 2-3C, 2-3F, 2-3G). Dartmouth's Route 6 well has been contaminated as a result of a former waste disposal site nearby and has been deactivated.

If surrounding monitoring wells (general location shown on Figure 4-1) show an improvement in water quality, this public well may be reactivated. A proposed well site exists just south of the new well at Russell Mill Road.

Dartmouth also has a Water Resource Council and Aquifer Protection District. The town owns large parcels of land surrounding all town wells, except for the Route 6 well.

The town of Fairhaven has several well fields and also buys about 1.0 MGD from New Bedford. The Fairhaven well sites are shown on Figure 2–3E. The Mill Road well field consists of 30 tubular wells, which may dry-up during a hot, dry summer. Tubular well fields are a series of 2.5-inch-diameter driven wells which are connected by a suction line that collects the combined yields. Another tubular well field, Fairhaven 2, with 40 individual wells, exists just north of Fairhaven Road. Water produced from these two wellfields is chlorinated. The Fairhaven Wolf Island Road field consists of three gravel pack wells, located in Rochester, whose water is treated for iron removal. The town of Fairhaven also has a proposed well field, the Tinkham Lane Site, which is south of the town's Wolf Island wells. It is likely no water treatment will be necessary. There are also homes with private wells in isolated areas of Fairhaven, such as West Island.

The Marion Water Department has a tubular well field in the town of Marion, south of Rochester Road. In addition, the Mary's Pond tubular well field is located in Rochester, on the east bank of Doggett Brook. The Marion East and Marion West gravel pack wells are located just south of the Mary's Pond field. A fourth gravel pack well is north of Wolf Island Road. Marion also has the New Bedford Road proposed well site in Rochester, located north of Perry Hill Road and east of Cushman Road. None of the Marion wells need treatment. The Marion well sites are shown on Figure 2–3E.



BASE MAP IS A PORTION OF THE U.S.G.S. FALL RIVER EAST, MA QUADRANGLE (7.5 MINUTE SERIES, 1978) AND THE WEST-PORT, MA QUADRANGLE (7.5 MINUTE SERIES, 1977). CONTOUR INTERVAL 10'.

AND MONITORING WELL FIELD

NEW BEDFORD HARBOR STUDY, NEW BEDFORD, MA

SCALE: 1" = 2000'

FIGURE 4-1



The Mattapoisett Water Company has one abandoned well, three producing stations, and two well fields under development (Figure 2-3E). Mattapoisett Well No. 1, located south of Rt. 195, has been abandoned. Mattapoisett Well No. 2, a tubular well feld, is located west of Acushnet Road and south of a large cranberry bog. Station Nos. 3 and 4 consist of gravel pack wells, located just south of Tinkham Lane. The existing wells are not treated. The two well fields under development are known as fields 11-6 and 11-2. The former will consist of three 8-inch test wells, located just north of the existing Mattapoisett wells. This field is expected to go on-line in the year 2000 and to yield 2.1 MGD. The second well site consists of a 2.5-inch test well located south of the existing Mattapoisett wells. Preliminary studies indicate high iron and manganese concentrations.

Mattapoisett is also connected with the Marion and Fairhaven systems in case of a water emergency. In addition, the towns of Mattapoisett, Fairhaven, Rochester, and Marion have formed the Mattapoisett River Water Supply Protection Advisory Committee.

5.0 WATER QUALITY IN THE STUDY AREA

5.1 <u>Influences On Natural Water Quality</u>

The source of most dissolved ions in water is the mineral assemblage in the rocks near the ground surface (Hem, 1970). The rate at which the ions in the minerals enter into solution depend on the purity and crystal size of the minerals, the texture and porosity, the degree of fissuring, and the length of previous exposure to the weathering process. The rate and extent of rock weathering is strongly influenced by temperature and the amount and distribution of precipitation. For instance, climates with alternating wet and dry seasons may favor weathering reactions that produce a large seasonal variation in the amount of soluble inorganics. In this climate, such as in the study area, the water quality fluctuates and the streams may have a wide range of chemical composition. In addition, climatic patterns tend to produce characteristic plant communities and soil types. Therefore, the composition of water draining from such areas will be different.

Man-made activities can affect the water quality in many different ways. For instance, contamination of water occurs through waste disposal and discharge, septic discharge, agricultural and household chemical use, highway deicing, and salt-water intrusion from excessive pumping.

5.2 General Water Quality Characteristics in the Study Area

Wiley, Williams, and Tasker (1978) of the USGS have characterized the water quality of the study area on a general basis. Individual contamination problems will be described in a later section. Long-term records of chemical analysis do not show any trends in water quality; however, high iron and manganese concentrations and color levels have always been a problem in local areas. The U.S. Public Health Service's recommended limits (1962) for iron and manganese in drinking water are 0.3 mg/l and 0.05 mg/l, respectively. Levels above these standards occur regularly in some wells, intermittently in some, and seldom in others. Iron and manganese concentrations in streams commonly exceed the recommended limits. After many years of pumping, several wells (e.g., Fairhaven's Mattapoisett station) have

experienced a sudden increase in iron and manganese, which may be associated with induced infiltration of surface water.

The quality of the surface water and groundwater is generally adequate for public supplies and industrial use, except when iron, manganese, and color levels are excessive. The water is generally soft (less than 60 mg/l as calcium carbonate), has a pH near 6.0, and is corrosive to metal. A narrow zone of salt-water intrusion may occur under heavy pumping conditions or when flooding exists along the coast. For instance, a municipal well within this area is Fairhaven's Mattapoisett River Station (Williams, Tasker, 1978).

5.3 Known And/Or Suspected Contamination Problems

Although the quality of groundwater and surface water is generally suitable for public supplies, several potential and/or existing water quality problem areas have been identified within the study area. The contamination problems were discovered during routine public supply sampling, USGS and private water resource studies, pumping tests, and USEPA Superfund waste disposal site investigations. In addition, miscellaneous water quality problems in domestic wells have been reported to the Massachusetts DEQE.

Groundwater quality has been investigated and monitored in the vicinity of three well-known disposal areas: Sullivan's Ledge and the New Bedford Municipal Landfill, both in New Bedford, and the Route 6 contaminated well field in Dartmouth. The two New Bedford sites are located adjacent to Apponagansett Swamp, which serves as a source of recharge to the aquifer associated with the drinking water wells in Dartmouth.

The New Bedford Landfill occupies 40 acres of marsh outside of the city. It is situated over an aquifer that is the source for the Dartmouth muncipal wells. The landfill has been used as a repository for domestic, commercial, and industrial wastes. Prior to 1971, incinerator ash containing unknown quantities of PCB residue was buried there. Liquid PCB wastes and other hazardous substances also may have entered the landfill since its inception. Historically, over one-half

million pounds of solid PCB wastes may have been disposed in the muncipal landfill. The New Bedford Municipal Landfill remains an active facility, but it is likely to be filled to capacity in the next few years.

EPA sponsored a study in 1978 which documented contamination of less than 1 part per billion (ppb) PCB in shallow groundwaters to the immediate north of the landfill. No contamination within detectable limits was found to the west, northwest, and east of the site. Subsequent studies were conducted in 1980 and 1983. In addition to PCBs, aqueous samples were also tested for volatile organics, pesticides, and extractable organics. Soil samples were also analyzed. The groundwater analyses showed trace levels of several chlorinated solvents and PCBs at the landfill. Only trace levels of two organic pesticides were found in the adjacent Shawmut Brook. Surface water samples taken near the landfill and in the swamp did not show detectable levels of PCBs. The studies concluded that the New Bedford Municipal Landfill is not currently a significant source of hazardous contaminants to the Paskamansett River system or the Apponagansett Swamp, since there is an apparent lack of contaminant migration off site.

At the request of EPA, NUS reviewed the previous studies and other existing information to assess whether the conclusions of the previous studies were justified. The NUS findings are detailed in a separate report and are summarized as follows:

- A shallow contaminant plume appears to be present in many directions from the landfill, and the existing wells that exhibited no contamination were likely screened below the principal plume.
- The peat layer thought to prohibit the vertical migration of contaminants beneath the landfill is likely not continuous. Zones of no peat have been documented.

- The proposal that historical deposits of PCB-contaminated waste are now buried beneath tens of feet of solid waste, and are thus not susceptible to leaching, may not be without exception. There is still visual evidence of chemical waste disposal at the landfill surface.
- Areas of intense liquid waste disposal in previous years have been identified. These areas are susceptible to offsite migration.

It is expected that EPA will initiate further investigations of the New Bedford Municipal Landfill. These may be performed in conjunction with either the Sullivan's Ledge Remedial Investigation and Feasibility Study or the expected closure studies for the landfill.

A much more significant contamination problem has been documented at Sullivan's Ledge. This site is approximately 10 acres in size and is located between the Route 140/195 interchange, Hathaway Road, and the New Bedford Whaler Inn property. It was originally operated as a granite quarry, but the property was later taken and managed by the City of New Bedford as a waste disposal site. Construction and demolition materials, rubber tires, junk cars, oils, sludges, reject capacitors, reject transformers, and miscellaneous chemical wastes were disposed there. Today the site is no longer used as a waste landfill, and it has been completely filled and graded.

Studies on the site indicate that industrial waste in the quarry is supplying PCB and organic contaminants directly to groundwater that has a potential to flow through fractured bedrock to wells or other points of surface discharge. The contaminated surface soils at the Sullivan's Ledge Site are subject to erosion into nearby streams during storm events. Elevated levels of numerous toxic contaminants have been detected in both surface water and groundwater at points more than 1,000 feet offsite to the northwest. It is likely that these contaminants are entering the Apponagansett Swamp, which in turn feeds the Paskamansett River system upstream from the Dartmouth wells. A detailed investigation of the Sullivan's Ledge Site is in progress by NUS.

An illegal hazardous waste disposal activity was responsible for the contamination and subsequent closure of Dartmouth's Route 6 municipal well in April, 1979. An illegal drum burial site (approximately 1000 drums) was discovered approximately 1500 feet from the municipal well. The barrels were removed and the contaminated soils spread thin to aerate. These remedial measures, however, did not prevent the contamination of the well (Special Legislative Commission on Water Supply, 1981).

Initially, chloroform and dichloroethylene were the identified contaminants in the municipal well. The consulting firm of Fay, Spofford, and Thorndike, Inc. installed 15 monitoring wells to determine the direction of groundwater and contaminant movement. All of the wells are located within an 1800-foot radius west and north of the Route 6 well. The location of the monitoring well field is shown in Figure 4-1. As of June 1983, 1,1,1-trichloroethane, chloroform, and trans-1,2,-dichloroethylene were found in the Route 6 well in concentrations ranging from a trace amount to 35 micrograms/liter (μ g/l). The following contaminants were detected in all or some of the monitoring wells in February and/or June 1983:

February, 1983

Contaminant	Monitoring Wells	Range in µg/l
Benzene	2,4,7,13,14	Trace - 36
Chloroform	1,3,5,7,9,10,11,13	Trace - 120
1-1-Dichloroethane	3,4,10,12,13,14,16	Trace - 100
1-2-Dichloroethane	14	80
Methylene Chloride	3,7,10,12	40 - 400
Tetrachioroethylene	2,12,14	Trace - 110
Trans-1,2-Dichloroethylene	2,4,8,14	Trace - 3170
Toluene	2,7,14	96 - 9800
1,1,1-Trichloroethane	2,3,4,8,10,12,13,14	32 - 980
Trichloroethylene	2,3,4,12,13,14	Trace - 285

June 1983

Contaminant	Monitoring Wells	Range in µg/l
Benzene	2	20
Chlorobenzene	2	Trace - 10
Chloroform	Route 6 well	22*, 24
Ethylbenzene	2	92, 180
1-1-Dichloroethane	2,4	16-295
1-2-Dichloroethane	2,4,5,7	Trace-100
1,1 Dichloroethylene	2,4	20-57
1,2 Dichloropropane	7	Trace, 10*
Tetrachioroethylene	2,4	19-90
Trans-1,2-Dichloroethylene	2,4,Route 6 well	Trace-2300
Toluene	2	1300, 2580
1,1,1~Trichloroethane	2,4,5,7,Route 6 well	42-1500
1,1,2~Trichloroethane	2,4,7	Trace
Trichloroethylene	2,4	20-255
Vinyl chloride	2	Trace
Xylenes	2,4	Trace-750

Reference for analyses: Fay, Spofford, Thorndike, Inc.

Detection Limit = 1 µg/l

As part of the Mattapoisett River Aquifer study, USGS personnel sampled seven observation wells and three surface water gaging stations in August 1981 and July 1982. These samples were analyzed for major constituents, pesticides, insecticides, and volatile organic compounds. In addition to elevated iron, manganese, and occasionally chloride and sodium concentrations, several organic contaminants were found at a river station and in four wells. Not all compounds were found at each location. However, the concentration levels were at or slightly above the detection limits. The following compounds were found (Olimpio, deLima, 1984):

^{*} Replicate analyses

Diazinon - agricultural insecticide

2,4-D - broadleaf, herbicide

DDT - insecticide

Dieldrin - insecticide

Benzene - solvent

1,2-Dichloroethane - solvent

Methylene Chloride - solvent

The presence of diazinon was not unexpected, because of the agricultural activity in the valley. The concentrations of the solvents benzene and methylene chloride, and of the herbicide 2,4-D, were below the maximum Ambient Water Quality Criteria levels established by the EPA (November 1980). Maximum levels have not been set for the solvent 1,2-dichloroethane or the insecticides DDT, diazinon, and dieldrin (Olimpio, deLima, 1984). Since the contaminants were not widespread and in low concentrations, it is likely that much of the contamination is due to agricultural or home use of the chemicals.

In 1980, the Massachusetts DEQE instituted the SPOT (State Purgeable Organic Testing) check program, which included analyzing municipal well fields for purgeable organic contamination. The following contaminants were tested for: methylene chloride, chloroform, bromodichloromethane, tetrachloroethylene, 1,1-dichloroethylene, 1,2-dichloroethane, trichloroethylene, 1,1-dichloroethane, 1,1-trichloroethane, dibromochloromethane, 1,2-transdichloroethylene, carbon tetrachloride, and bromoform.

None of the compounds were detected in the Mattapoisett, Dartmouth and Marion municipal well systems; however, methylene chloride and bromodichloromethane were detected in the Fairhaven tube well system near River Road. In the Fairhaven Naskatucket Mill tube well system, methylene chloride, chloroform, and dibromodichloromethane were detected. In all cases, none of the contaminants were in concentrations exceeding $5.8~\mu g/l$ (ppb). (DEQE SPOT Test Analyses, 1980).

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- 5. Jeffrey Osuch, Fairhaven Water Department, February 1, 1984
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- 7. Paul Anderson, MADEQE, Lakeville, April 9, 1984
- 8. Joe Conley, Massachusetts MADEQE, Lakeville, April 24, 1984.

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APPENDIX A

MASSACHUSETTS DRINKING WATER QUALITY REGULATIONS

A.1 <u>Massachusetts Drinking Water Regulations, 310 Code of Massachusetts</u> Regulations (CMR) 22.00

The Massachusetts Drinking Water Regulations, 310 CMR 22.00, effective September 30, 1983, specify maximum contaminant levels allowable in public drinking water, frequency of sampling, and analytical techniques. The regulations distinguish between a public water system and a nonpublic system. The former system is one in which water is piped for human consumption, has at least 15 service connections, and serves an average of at least 25 individuals daily for at least 60 days a year.

A public water system is either a community system or a noncommunity system. The former system serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents. A noncommunity system means a public water system that is not a community system. The standards for coliform bacteria, inorganic, organic, turbidity, and radionuclide contaminants are described below.

The number and frequency of required coliform samples depend on whether the public system is community or noncommunity and how many people are serviced. The maximum allowable contaminant level may be calculated in several ways using the membrane filter or fermentation tube tests. Community samples must be taken at least monthly. Noncommunity systems must be sampled for bacteria at least once every calendar quarter during which the system provides water to the public.

When a membrane filter is used, the maximum coliform bacteria count is one per 100 milliliters (ml) when the arithmetic mean of all monthly samples is used. If less than 20 samples are taken, the limit is 4 per 100 ml in more than one sample. If more than 20 samples are examined each month, the limit is 4 per 100 ml in more than 5 percent of the samples.

When the fermentation tube analytical method is used, the maximum level has been reached when bacteria is found in more than 10 percent of the portions in any month. If less than 20 samples are examined, the maximum level occurs when three or more portions are found in more than one sample. When 20 or more samples are taken, maximum levels are reached when bacteria appears in three or more portions in more than 5 percent of the samples.

Community systems using all or part surface water resources must be sampled annually for metals. The community systems using only groundwater supplies must be sampled once every 3 years. These standards do not apply to noncommunity systems. The metals include arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, flouride, iron, and manganese.

Sodium and nitrate must be tested every year in a community system that uses any surface water. The frequency of testing for both substances decreases to once every 3 years where groundwater supplies are used exclusively. Should the sodium concentration exceed 15 mg/l in a surface water or groundwater supply, the supply must be tested for sodium on a quarterly basis. Noncommunity supplies must be tested for sodium at 3-year intervals; however, they also must be tested quarterly if concentrations exceed 15 mg/l. The DEQE will specify the frequency for nitrate analysis in noncommunity supplies.

All community systems using surface and/or groundwater must be analyzed for total trihalomethanes on a quarterly basis. The DEQE may permit groundwater systems to be analyzed for this parameter less frequently on an individual basis.

The following radionuclides are monitored on a quarterly basis: radium 226, 228, gross alpha particle activity, tritium, and strontium 90. The latter two radionuclides are optional analyses, depending upon DEQE requirements. In addition, the DEQE may require analysis for other man-made radionuclides, should their occurrence in the water supply be suspected.

Community systems using surface water supplies must also analyze for chlorinated hydrocarbons and chlorophenoxy particles at least once every 3 years. The frequency and need of sampling for community systems using only groundwater is specified by the DEQE.

Tables A-1 through A-3 list the maximum allowable contaminant levels for all parameters discussed herein..

TABLE A-1

MASSACHUSETTS MAXIMUM CONTAMINANT LEVELS FOR INORGANICS REGULATION 310 CMR 22.06

Contaminant	Maximum Contaminant Level (mg/l)				
Arsenic	0.05				
Barium	1.0				
Cadmium	0.010				
Chromium (+6)	0.05				
Lead	0.05				
Mercury	0.002				
Selenium	0.01				
Silver	0.05				
Fluoride (Based on Temp °F)					
53.7 & Below	2.4				
53.8 to 58.3	2.2				
58.4 to 63.8	2.0				
63.9 to 70.6	1.8				
70.7 to 79.2	1.6				
79.3 to 90.5	1.4				
Sodium	20				
Nitrate	10 Community				
	20* Noncommunity				
Iron	0.3**				
Manganese	0.05**				

^{*} Water must not be available to children under 6 months. Nitrate levels above 10 mg/l must be posted.

^{** 1962} Public Health Service Recommended Limits

TABLE A-2

MASSACHUSETTS MAXIMUM CONTAMINANT LEVELS FOR CHLORINATED HYDROCARBON AND CHLOROPHENOXY PESTICIDES REGULATION 310 CMR 22.07

	Contaminant	Maximum Contaminant Level (mg/l)
A)	Chlorinated Hydrocarbons:	
	Endrin	0.0002
	Lindane	0.004
	Methoxychlor	0.1
	Toxaphene	0.005
B)	Chlorophenoxys:	0.1
	2.4.5 - TP Silvex	0.01

TABLE A-3

MASSACHUSETTS MAXIMUM CONTAMINANT LEVELS FOR TRIHALOMETHANES, TURBIDITY, RADIONUCLIDES REGULATIONS 310 CMR 22.08, <u>22.09</u>

	Contaminant	Maximum Contaminant Level				
	Total Trihalomethanes	0.01 mg/l*				
	Turbidity	1 Turbidity Unit				
	Combined Radium 226 and Radium 228	5 PCi/I**				
(\$.	Gross Alpha Particle Activity, Including Radium 226	15 PCi/I**				
	Tritium	20,000 PCi/I				
	Strontium-90	8 PCi/I				
	All Other Man-made Radionuclides	Standard Found In National Bureau of Standards Handbook 69				

PCi/l = picocuries per liter

^{*} Mean of quarterly samples

^{**} Analysis made on composite of four consecutive quarterly samples or the average analysis of four samples

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Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment*

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Abstract-Polychlorinated biphenyls (PCBs) were measured in interstitial waters and sediments at a site in New Bedford Harbor, Massachusetts, to study partitioning processes of hydrophobic organic compounds in marine sediments. Pore water concentrations of total PCBs, expressed as Aroclor 1254, increased with depth in the sediments with a maximum concentration of 17.1 µg/L at 9-11 cm. Apparent distribution coefficients of individual chlorobiphenyls decreased with depth and were related to dissolved organic carbon levels. Results from this site suggest that most of the PCBs in interstitial waters are sorbed to organic colloids. A simple three-phase equilibrium sorption model can explain many features of the data. Changes in the composition of individual chlorobiphenyls in the sediments were also apparent. Microbial degradation appears to be responsible for large relative depletions of several chlorobiphenyls with depth in the core.

INTRODUCTION

ESTUARINE AND COASTAL marine sediments act as short or long term reservoirs for many hydrophobic organic compounds (LEE et al., 1979; WAKEHAM and FARRINGTON, 1980; HITES et al., 1980; PRAHL and CARPENTER, 1983). Sorption reactions involving interstitial waters and sediment particles control the rates and mechanisms of transport of organic compounds within and out of sediments, and also affect the bioavailability of these compounds. Other diagenetic processes such as biological and chemical transformation reactions, diffusion, advection, and mixing and resuspension of the sediment bed, will also affect the distribution of hydrophobic organic compounds in sediments and pore waters (BERNER, 1980). The relative importance of each of these processes depends on the molecular structure, biological activity and physicalchemical properties of the individual organic compounds, as well as properties of the sedimentary environment.

We are studying PCBs (polychlorinated biphenyls) as model compounds to probe many of these processes. In addition, there are continuing environmental concerns with PCBs which require a better understanding of the fate of PCBs which have accumulated in surface sediments (NAS, 1979). PCBs are a mixture of 209 possible congeners which exhibit a wide range of physical and chemical properties. Their reported solubilities (MACKAY et al., 1980) and octanol-water partition coefficients (RAPAPORT and EISENREICH, 1984; WOODBURN et al., 1984) are representative of many hydrophobic organic compounds present in the marine environment. PCBs were widely used as industrial chemicals in the United States because of their thermal and chemical stability. The production and regulatory histories of PCBs, and estimates of their sources and transport pathways in the environment have been re-

viewed (NISBET and SAROFIM, 1972; NAS, 1979). PCBs are characterized by slow rates of chemical and biological degradation in the aquatic environment (NAS, 1979). PCB measurements in the field have been used in the study of particle-seawater partitioning (DEXTER and PAVLOU, 1978a), sediment transport in the Hudson River (BOPP, 1979, BOPP et al., 1981), and the associations and transport of PCBs with particles in the Great Lakes (EISENREICH et al., 1983, EADIE et al.,

Several chlorobiphenyls along with many other hydrophobic organic compounds have been utilized in laboratory sorption experiments with various sediments and soils (KARICKHOFF et al., 1979; MEANS et al., 1980; SCHWARZENBACH and WESTALL, 1981; CHIOU et al., 1983). Laboratory studies have also quantitatively shown the importance of the partitioning of hydrophobic organic compounds with estuarine colloidal organic matter (MEANS and WUAYARATNE, 1982, WUAYARATNE and MEANS, 1984a). LANDRUM et al. (1984) measured partition coefficients for two polychlorobiphenyls with natural dissolved organic matter, and HASSETT and ANDERSON (1982) showed a reduction in the sorption of 2,2'-5,5'-tetrachlorobiphenyl to particles on addition of colloidal organic matter.

Predictions of partitioning of hydrophobic organic compounds based on experimental data are largely untested in the field. We report here an investigation of the partitioning of PCBs between the sediments and interstitial waters at a coastal marine site. This site is located in New Bedford Harbor (the Acushnet River Estuary) in southeastern Massachusetts. New Bedford Harbor has been heavily impacted by PCB pollution. The nature of this contamination has been recently reviewed (Weaver, 1984; Farrington et al., 1985).

SAMPLING SITE AND METHODS

The sediments and interstitial waters were obtained from a large volume box core taken from the R/V Asterias at Station

67 of SUMMERHAYES et al. (1977) in the outer harbor of New

Woods Hole Oceanographic Institution Contribution No. 5839.

Bedford on September 1, 1983. This site, in 8 to 9 meters of water, has sediments which are characterized as organic rich (4-6% organic carbon), silty mud with occasional shell fragments. This location borders Butler's Flat and the navigation channel of the outer harbor. The sediment accumulation rate at this site is not known. SUMMERHAYES et al., (1977) report that the sedimentation in this general area probably averages 2-3 mm/yr, but that the rate of sediment accumulation of the dredged navigation channel appears to be about 4 cm/yr. These workers report that the sediment accumulation in all of New Bedford Inner Harbor appears to have increased 5 to 10 fold since the construction of a hurricane barrier, which was completed in 1966, separating the inner and outer harbor. A minimum estimate of 1.0 cm/yr for a sediment accumulation rate at this site can be set from the presence of PCBs at the bottom of this 41 cm core, provided that the PCBs have not penetrated the sediment by some other mixing or migrational process. PCBs were first used in New Bedford in 1941 (WEAVER, 1984).

Sampling methods for the sectioning of muds and subsequent extraction and filtration of pore water employ inert atmosphere techniques. These methods, summarized here, are described by SHOLKOVITZ and MANN (1984) and are only slightly modified for trace organic analysis. A Sandia-Hessler Type MK3 sediment corer with a 0.25 m² by 70 cm box was used. The water overlying the sediment was siphoned off immediately after the core was brought on board. The sedimentwater interface was undisturbed and a plexiglass sheet was placed over the surface of the mud. The small amount of headspace was purged with freon (Genetron 22) to minimize air penetration. Within two hours the box core was removed from its frame at the dock and transported for sectioning and pore water extraction. Sectioning was performed by replacing one side of the coring box with 18 interlocking, 2 cm wide plexiglass plates which allowed sectioning of 2 cm sediment horizons with a teflon coated, metal sliding sled. Each horizon was immediately transferred to a N2 filled glove box and loaded into acid and acetone cleaned, I liter polypropylene centrifuge bottles. Four to six bottles were filled and centrifuged at about 3500 rpm (~3500 g's) for 20 minutes in a IEC model 6000 model centrifuge. The temperature was controlled at 20°C. The temperature of the mud was 20.5°C at sampling and did not change appreciably during sectioning. Centrifugation resulted in the extraction of 0.80 to 1.7 liters of pore water per 2 cm horizon, representing 38 to 56% of the water content in these sediments. The pore water was subsequently filtered under vacuum while continuously bubbling with N2. Precombusted, 142 mm Gelman Type AE glass fiber filters, which have a nominal pore size of I μm , were used. The loss of PCBs from interstitial waters as a result of volatilization during vacuum filtration and a N2 purge is expected to be minimal. The fraction of dissolved chlorobiphenyls lost from N₂ purging can be calculated as follows:

fraction chlorobiphenyl lost = $1 - C/C_0 = 1 - e^{-(H \times b \times \iota/V)}$

where H' (mL/cm³) is the Henry's law constant for individual chlorobiphenyl in seawater, b is the flow rate of N₂ (cm³/min.), t is the time and V is the volume of pore water filtered. A maximum of 0.2 to 2.0% loss is calculated from a Henry's law constant of 0.01 mL/cm³ (MURPHY et al., 1983) and the experimental conditions used, and would be reduced by lower activities of PCBs in solution due to associations with dissolved organic matter.

Small subsamples of pore water were saved for analysis of dissolved organic carbon (DOC), SO₄. Fe and Mn, and salinity. The remainder of the sample was then stored in glass along with 75 ml of CH₂Cl₂ for later analysis of PCBs. Subsamples of sediment were recovered from the centrifuge bottles, combined, and stored frozen in glass for later PCB and CHN analyses. A total of 41 cm of sediment depth were analyzed as 17 sections. Sectioning, extractions and filtrations were completed in approximately 12 hours.

ANALYTICAL METHODS AND CALCULATIONS

Standard techniques were used to determine pore water constituents. DOC was analyzed by a wet persulfate oxidation method adapted from STAINTON (1973). Sulfate was determined by barium sulfate precipitation, Fe and Mn by atomic absorption spectrometry, and chlorinity by AgNO₃ titration. Approximate precisions of these methods were 3, 2, 2, 4, and 0.7% respectively. Water content was determined after heating wet sediments to a constant weight at 110°C. CHNs of dry sediments, which had been treated with 10% HCl to remove small amounts of carbonate, were measured on a Perkin-Elmer CHN Analyzer.

The isolation and quantification of PCBs were as follows. Immediately prior to solvent extraction, both sediments and pore waters were spiked with an internal standard consisting of 2,4,5-trichlorobiphenyl and 2,2',3,4,5,6'-hexachlorobiphenyl. The corresponding IUPAC numbers for these compounds are 29 and 143 respectively (BALLSCHMITER and ZELL, 1980). These two chlorobiphenyls do not occur in appreciable amounts in the industrial mixtures of PCBs and are used to monitor procedural recoveries and as quantification standards. Wet sediments were Soxhlet extracted for 24 hours with 350 ml of 1:1 hexane:acetone. An additional 24 hour extraction of sediments with fresh hexane:acetone gave $8.2 \pm 3.0\%$ of. the individual chlorobiphenyls determined the previous day, and no additional recovery of spiked compounds. Pore waters were extracted in separatory funnels, shaking for 1.5 minutes, three times with 75 ml of CH₂Cl₂ and about 100 mg of sodium lauryl sulfate added to control emulsions. A fourth 5 minute pore water extraction yielded another 0.61 ± 0.10% of individual PCBs. These additional yields do not affect the results and biogeochemical interpretation presented here. Extracts were separated from aqueous phases in separatory funnels, dried with anhydrous Na2SO4, and concentrated with Kuderna Danish concentrators. A hexane fraction containing PCBs was collected from silica gel (1% deactivated) using a layer of activated copper under the silica gel to remove reduced sulfur.

PCBs were analyzed from concentrated hexane extracts by high resolution capillary gas chromatography with electron capture detection on a Hewlett-Packard 5840 gas chromatograph with a 30 meter DB5 fused silica column (J&W Scientific) operated with H_2 carrier gas using the following chromatographic conditions: a 2.0 μ l splitless syringe injection; 2 minutes at 40°C followed by rapid heating to 120°C (hold until 5 minutes); temperature programming at 2°C/min to 230°C (60 min) and then 4°C/min to 270°C; makeup gas, 5% methane:95% argon at 30 ml/min.

All reagents were either solvent extracted or combusted, and solvents were distilled in glass. Procedural blanks were insignificant at the PCB levels of these samples except for a contamination problem in the 0-3 cm pore water sample where many of the higher molecular weight PCBs are not reported.

Several complementary methods were used to identify individual chlorobiphenyls in the industrial mixtures Aroclor 1242 and 1254, which are the source of PCBs in these samples (Aroclor 1242 and 1254 standards are Monsanto lot numbers AK-344 and AA-1 respectively). A significant portion of the PCBs used by the manufacturing plants in the area were actually Aroclor 1016 which is very similar in composition to Aroclor 1242 (NAS, 1979). Retention times of nearly 70 pure PCB standards (from Ultra Scientific and Analabs) were compared to those in the mixtures. GCMS spectra obtained with a Finnegan 4500 quadropole mass spectrometer coupled with a Carlo Erba 4160 glass capillary gas chromatograph confirmed the degree of chlorination of the various peaks. GC and GCMS identifications reported by other workers, using SE-54 and similarly coated columns, were consulted to obtain a consistent set of peak identifications (DUINKER and HILLEBRAND, 1983; MULLIN et al., 1984; EISENREICH et al., 1983; ALBRO and PARKER, 1979; ALBRO et al., 1981; and BALLSCHMITER and ZELL, 1980). The relative amounts of contributing isomers

in some unresolved peaks are still tentative, but this does not affect the identification of the chlorobiphenyls reported here.

Recoveries of internal standards 29 and 143 were 93.3 \pm 13.3 and 98.9 \pm 17.0% respectively for 16 sediment samples and, and 83.9 \pm 12.9 and 92.8 \pm 20.8% for 11 pore water samples. Five pore water samples from the 23-35 cm core sections were underspiked and no recoveries are reported. The error in recoveries is associated with variation in absolute detector response. However, except for the five underspiked pore water samples, relative responses of peaks to that of internal standard 143 were used. This resulted in precisions of better than 5%. Estimates of total PCBs as Aroclor 1254 were obtained by comparing the relative response of the 10 peaks of greatest area, A_i to that in a standard where the amounts of Aroclor 1254 (m_{1234}) and 143 (m_{143}) are known:

Aroclor 1254 (µg/g sample)

$$= \sum_{i=1}^{10} \frac{((A_i/A_{143})_3 \cdot (A_{143}/A_i)_{STD} \cdot (m_{1234}/m_{143})_{STD} \cdot (m_{143}\text{spike}))}{10 \times \text{wt. sample (g)}}$$

where m_{143} spike is the amount of 143 spiked as an internal standard to the sample, S refers to sample, and STD refers to a standard mixture of Aroclor 1254 with isomer 143 added. To estimate Aroclor 1242, the 6 largest peaks in the mixture which do not appear in Aroclor 1254 were used, and standard 29 was used as the internal standard. Representative chromatograms of Aroclor standards, and samples are illustrated in a later section (Fig. 2) along with the chlorobiphenyl identifications used in Aroclor quantifications (Fig. 2 and Table 2).

A total of 46 separate PCB peaks were quantified. In addition, only qualitative information for 5 dichlorobiphenyls

is presented because peak areas were too small for quantification. It is estimated that the precisions of the Aroclor calculations and other peak ratios are approximately 5% and that of apparent distribution coefficients, $K'_{\rm d}$, are therefore about 7%. $K'_{\rm d}$ is calculated as the sediment concentration of individual chlorobiphenyls in the sediments divided by that measured in the interstitial waters, and is in units of L/Kg. The concentrations and distribution coefficients of PCBs from the pore water sections between 23 and 35 cm are uncorrected for average recoveries and represent a lower limit in concentrations.

RESULTS AND DISCUSSION

Interstitial water and sediment characterization

Pore water profiles of Mn, Fe and SO₄ (Fig. 1A) reflect suboxic diagenesis in this core. The reaction sequence in the oxidation of organic matter in marine sediments has been well studied (FROELICH et al., 1979; ALLER, 1980a). The maxima of reduced Fe and Mn in the 0-3 cm section indicate oxygen depletion in this upper layer. The profile of sulfate suggests that sulfate reduction occurs near the surface and the smoothness of the profile indicates that oxygen is depleted throughout the core. The removal reactions of Fe with depth in this core do not appear to be as efficient as those for Mn. It is expected that the sulfide would be an effective sink for reduced Fe (ALLER, 1980b). A

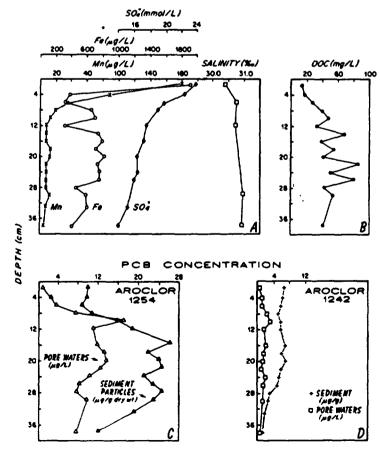


FIG. 1. (A-B) Interstitial water profiles of Fe, Mn, SO₄, salinity, and DOC. (C-D) Profiles of total PCBs as Aroclor 1254 and Aroclor 1242 in sediments and pore waters.

Table 1. Profiles of bulk sediment properties and Aroclor concentrations in sediments and pore waters.

						Arocler 1242		Aroclor 1254	
Dopth	1 H2O	TOC	100	C/M	DOC	Sed.	2.4.4	Sed.	P.V.
<u>(ca)</u>		(8)	(1)		(Be/L)	(ME/E)	(ue/L)	(ug/g)	(ug/L)
0-3	55.85	6.06	0.43	9.6	14.4	6.43	0.421	10.1	0.893
3-5	55.87	5.23	0.51	10	17.4	6.14	1.00	9.86	2.61
5-7	54.97	3.74	0.36	10	27.7	5.72	1.04	1.14	3.68
7-9	50.60	4.98	0.48	10	40.3	5.10	2.27	10.9	7.70
9-11	51.26	4.40	0.40	11	47.9	5.62	3.03	16.0	17.1
11-13	47.49	4.14	0.34	12	32.6	3.63	1.57	18.9	11.1
13-13	50.98	3.85	0.31	12	68.7				
15-17	52.50	4.02	0.32	13	39.2	6.77	1.98	26.2	11.8
17-19	53.22	4.74	0.39	12	55.1	5.49	1.40	21.9	13.4
19-21	53.42	4.98	0.40	12	42.0	6.84	1.20	23.9	13.7
21-23	55.71	5.96	0.53	ü	87.0	5.76	0.953	24.5	12.6
23-25	59.48	5.68	0.51	ü	50.9	5.09	1.80	21.0	10.4
25-27	57.98	4.78	0.41	12	81.4	4.62	1.33	22.8	8.35
27-29	54.98	4.86	0.42	12	43.7	2.81	0.522	24.5	7.83
29-31	44.95	5.33	0.43	12	54.2	2.40	1.17	22.8	9.84
11-35	45.67	3.45	0.35	16		1.66		19.1	
35-41	39.92	4.76	0.34	14	41.4	1.27	0.532	12.1	7.65

" Sed. " sediment, F.W. " pore water.

subsample of pore water from the 35-41 cm section also was filtered through a 0.40 μ m Nuclepore filter. This resulted in a 79% reduction of Fe in the filtrate, so that we infer an association of Fe with a colloidal phase. Near constant measurements of chlorinity (Fig. 1A) in this core indicate that groundwater advection is not measurable at this site.

The concentrations of DOC in the interstitial waters (Table 1) are consistent with the range of concentrations and depth profiles reported for other reducing nearshore marine sediments (NISSENBAUM et al., 1972; KROM and SHOLKOVITZ, 1977; HENRICHS, 1980; ELDERFIELD, 1981; HENRICHS and FARRINGTON, 1984; and SHOLKOVITZ and MANN, 1984). Krom and Sholkovitz showed that the increase in DOC with depth was due to an increase in colloidal organic matter. Several of these workers did UV and infrared spectroscopic studies of the colloidal organic matter, and found it to appear similar to melanoiden or marine humic substances (NISSENBAUM et al., 1972; KROM and SHOLKOVITZ, 1977; and ELDERFIELD, 1981).

The sediments at this site are enriched in total organic carbon (Table 1). The changes in organic carbon and water contents with depth indicate either changes in the source of organic carbon, non constant sedimentation or non steady-state diagenesis of organic carbon. It can also be seen that the C/N ratio increases steadily downcore with a local minima in the profile from 21-25 cm. This trend may represent preferential nitrogen metabolism or changes in the quality and quantity of natural organic matter supply.

PCB composition and concentrations

The composition of individual PCBs in the sediments is similar to a mixture of Aroclor 1242 and Aroclor 1254; Aroclor 1242 consisting primarily of di-, tri-, and tetrachloro biphenyls and Aroclor 1254 consisting of tetra-, penta-, hexa-, and heptachloro biphenyls. Differences in composition of PCBs between sediment samples at different depths, and between sediment and pore water at the same depth, are seen in Fig. 2. Surface sediments have a composition of

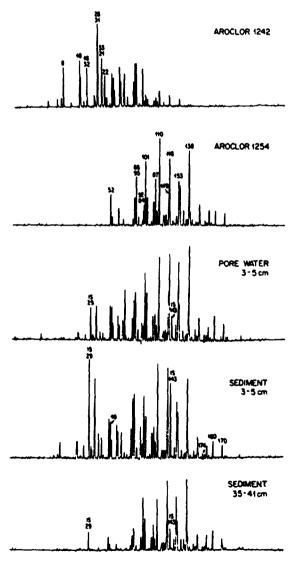


FIG. 2. Capillary gas chromatograms of PCB Aroclor standards, pore water and sediment samples from 3-5 cm depth, and the 35-41 cm sediment sample. Retention times increase along the x-axis. Chlorobiphenyl numbers indicate identification of peaks used in total Aroclor calculations and other chlorobiphenyls reported here (see Table 2).

Table 2. PCS IUPAC numbers and structures.

IUPAC	Stucture
	2,4'-dichlorobiphenyl
18	2.2'.5-trichlorobiphenyl
16).	2.2',3-trichlorobishenyl
32).	2.4',6-trichlorobiphenyl
26.	2.4.4'-trichlorobishemyl
jī)	2.4',5-crichlorobiphonyl
33,	2',3,4-trichlorobiphenyl
21	2,3,4-trichlorobiphomyl
22	2,3,4'-trichlorobiphonyl
49	2,2',4,5'-tetrachlorobiphenyl
52	2,2',5,5'-tetracklerobiphenyl
66)	2,3',4,4'-tetrachlerobiphenyl
95	2,2',3,5',6-pentachlorobiphenyl
44	2,2',3,5,5'-pentachlorobiphenyl
64)	2,2',3,3',6-pentachlorobiphonyl
101	2,2',4,5,5'-pentachlorobiphenyl
87	2,2',3,4,5'-pentachlorobiphonyl
110	2,3,3',4',6-pentachlorobiphenyl
149	2,2',3,4',5',6-hexachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
136	2,2',3,4,4',5'-hexachlorobiphenyl
153	2,2',4,4',5,5'-hexachlorobiphonyl
170	2,2',3,3',4,4',5-heptechlorobiphenyl
174	2,2',3,3',4,5,6'-heptachlorobiphenyl
180	2,2',3,4,4',5,5'-heptachlorobiphenyl

these chlorobiphenyls are not resolved by our GC analysis.

PCBs which is very similar to a mixture of the Aroclor 1242 and Aroclor 1254 standards shown, with somewhat lower concentrations of some of the more soluble di- and trichlorobiphenyls relative to Aroclor 1242. This could be the result of increased solubilization or degradation of those compounds either in the sediments or in the water column during transport to the sediment. There are smooth changes in the composition of PCBs in the sediments. The di-, tri-, and tetrachlorobiphenyls are depleted with increasing depth in the core, while the penta-, hexa-, and heptachlorobiphenyls maintain a nearly constant composition. The resulting compositions of PCBs are seen to resemble Aroclor 1254 quite closely with varying amounts and compositions of the lower chlorinated compounds which have little resemblance to Aroclor 1242 deeper in the core.

The profiles of Aroclors 1254 and 1242 in sediments and interstitial waters (Figs. 1C and 1D; Table 1) illustrate the increase in pore water concentrations of PCBs with increasing depth in the core. The concentrations of Aroclor 1254 in interstitial waters are highly elevated, 0.893 to 17.1 μ g/L, and exhibit a maxima in the profile at a depth of 9-11 cm. These concentrations can be compared to water column concentrations of 11 to 20 ng/L at a nearby station in the outer harbor (BROWNAWELL and FARRINGTON, 1985). They can also be compared to reported solubilities of Aroclor 1254 in seawater of 4.36 µg/L (DEXTER and PAVLOU, 1978b) and 24.7 μ g/L (WIESE and GRIFFIN, 1978). The concentrations of many of the higher chlorinated, less soluble, compounds exceed the reported solubilities of chlorobiphenyl isomer groups in a mixture of Aroclor 1254 in seawater (DEXTER and PAYLOU, 1978b). EADIE et al. (1983) have reported elevated concentrations of pore water PCBs in 3 Lake Michigan surface sediments. Total PCB concentrations of 0.159-0.342 µg/L were reported in interstitial waters of sediments of much

lower total PCB concentration (63.5 to 160 ng total PCB/g sediment). Unlike these sediments, the Lake Michigan pore waters were greatly enriched in Aroclor 1242. DUINKER and HILLEBRAND (1979) have measured PCB concentrations of 10-40 ng/L in the interstitial waters of sediments from the Rhine-Meuse Estuary.

The sediment concentrations of Aroclor 1254 also increase between the 7-9 and 15-17 cm sections, but this increase is not nearly as dramatic as that in the pore waters. Aroclor 1242 (Fig. 1D) makes a substantial contribution to the total PCBs in the surface sections and gradually diminishes in importance with depth. The PCBs in pore waters at this site are enriched in the more highly chlorinated isomers and Aroclor 1242 type compounds occur in lower amounts. However, concentrations of Aroclor 1242 in interstitial waters are also elevated above water column values of 17 to 32 ng/L (BROWNAWELL and FARRINGTON, 1985.)

The profile of DOC (Fig. 1B) can be compared to either the profile of Aroclor 1254 or total pore water PCBs (Aroclors 1242 + 1254). The similarity of these profiles, especially over the upper 13 cm, is suggestive of an association of PCBs with dissolved organic matter. The apparent supersaturation of many chlorobiphenyls in pore waters is consistent with this hypothesis.

Partitioning of PCBs between sediments and interstitial waters

The composition of PCBs in the pore waters is similar to that of the sediments at each depth interval although the more highly chlorinated congeners generally are enriched in the interstitial waters when compared with the sediment phase. The partitioning of PCBs between the sediments and interstitial waters is certainly important in evaluating the diagenetic processes and remobilization of PCBs in sediments. The measured distribution coefficients of individual chlorobiphenyls can also be used to study sorption processes of hydrophobic organic compounds in natural marine sediments and to evaluate the role of dissolved and particulate organic matter on the observed partitioning. Sorption reactions of these compounds with fresh water sediments and soils have been extensively studied using laboratory experiments. It has been demonstrated that sorption of neutral, relatively non-polar compounds correlates well to the organic carbon content of the sorbent (KARICKHOFF et al., 1979; MEANS et al., 1980; and SCHWARZENBACH and WESTALL, 1981). These workers found that an organic carbon normalized partition coefficient, K_{∞} , is a good predictor of partitioning for a given hydrophobic organic compound onto a wide range of sediments and soils, at $f_{\infty} > 0.001$:

$$K_{\rm oc} = K_{\rm p}/f_{\rm oc}$$

where K_p is the partition coefficient determined from the linear sorption isotherm determined experimentally and f_{∞} is the fraction organic carbon. The organic carbon fraction has also been shown to control the sorption of DDT with marine sediments (PIERCE et al., 1974) and to influence the partitioning of PCB Aroclor 1254 onto a variety of marine derived substrates (HIRAIZUMI et al., 1979). Several investigators have shown that $\log K_{\infty}$ varies inversely with the logs of water solubilities and directly with log octanol-water partition coefficients of a wide range of solutes, encompassing greater than seven orders of magnitude in aqueous solubilities (CHIOU et al., 1979; KARICKHOFF et al., 1979; SCHWARZENBACH and WESTALL, 1981; and MEANS et al., 1980). These relationships have been shown to hold for compounds having solubilities as low as many of the hexachlorobiphenyls. A solvent-water partitioning model has been presented to describe sorption behavior of nonionic organic compounds with soils and sediments (CHIOU et al., 1979; CHIOU et al., 1983).

The presence of natural DOC has been shown to decrease the apparent sorption of fatty acids onto bentonite in seawater (MEYERS and QUINN, 1973) and to decrease the adsorption of dieldrin onto aquifer sand (BOUCHER and LEE, 1972), and cholesterol and tetrachlorobiphenyl onto suspended particles (HASSETT and ANDERSON, 1982). POIRRIER et al. (1972) and CARTER and SUFFETT (1982) both demonstrated high partitioning or binding affinity of colloids and humic acids with DDT. HASSETT and ANDERSON (1979, 1982), MEANS and WIJAYARATNE (1982) and WIJAY-ARATNE and MEANS (1984b) suggest that it is the operationally defined high molecular weight or colloidal fraction of DOC which is important in partitioning. Finally, estuarine colloidal organic matter has been shown to have relatively high partition coefficients with two herbicides and three polycyclic aromatic hydrocarbons (PAH) (MEANS and WIJAYARATNE, 1982; WIJAYARATNE and MEANS, 1984a). These studies suggest that the partitioning of hydrophobic organic compounds with natural organic colloids may be similar to that of sedimentary organic matter.

On the basis of results from the above studies and the high DOC levels in this core, we propose that a significant fraction of all the chlorobiphenyls present in pore water solution are associated with organic colloids. For the purposes of discussion, we have assumed that the concentration of organic colloids is reflected by the DOC profile, which is a reasonable assumption based on the work of KROM and SHOLKOVITZ (1977). Thus, measured distribution coefficients of PCB isomers or components are treated as apparent distribution coefficients

$$K'_{d}(L/kg) = \frac{S(\mu g/kg)}{D + C(\mu g/L)}$$
(1)

where S, D, and C are the concentrations of PCB components in the sediment or solid phase, dissolved and colloidal phases, respectively.

Profiles of K'_4 for 51 resolved and unresolved chlorobiphenyls have been generated and all show a decrease over the upper 11 cm and remain low deeper in the core. Examples of K'_d are given in Table 3, and selected profiles are illustrated in Fig. 2. K'_d values of individual chlorobiphenyls range from about 5×10^2 to 2 × 10⁴ and are considerably lower than water column K'_d measurements of PCBs in Puget Sound (DEXTER and PAVLOU, 1978a, PAVLOU and DEXTER, 1979), the Hudson River (BOPP, 1979), Lake Superior (EISENREICH et al., 1983) and several other environments where the role of colloids may not be as great, due to lower concentrations of DOC and correspondingly lower concentrations of colloids. K'_d values ranged from 10⁴ to 10⁷ in those studies. EADIE et al., (1983) also report similarly low K'_d values, 248 to 7000, for PCBs in the interstitial waters of Lake Michigan. The elevated concentrations of PCBs, low K'as, and correlation of these properties with DOC (Fig. 3 compared to Figs. 1B, C and D) strongly implicate a considerable colloidally associated PCB phase in this sediment, even for the more soluble trichlorobiphenyls.

The role of both colloidal and sedimentary organic matter can be further evaluated by comparing a simple three-phase equilibrium sorption model, in which both colloidal and sediment bound phases exist in a dynamic

Table 3. Apparent distribution coefficients (K'g) of ten polychlorizated hiphenyls with decreasing depth in the sediment. Stuctures corresponding to the IUPAC chlorobiphenyl numbers are found in Table 2. A complete data set of the K'gs of all 46 resolved and unresolved chlorobiphenyls can be obtained from the authors.

K. ⁴ ×10 ₋₃ (T/K ⁶)										
Ca)	18	28+31	49	52	101	110	138	153	170	180
0-3	14.3	24.7	11.3	12.3	11.6	13.2	•	•	•	•
3-5	5.32	8.00	3.66	4.11	3.63	4.46	3.14	3.42	2.62	2.35
5-7	3.12	5.60	2.77	2.84	2.17	2.62	2.06	1.00	2.20	1.97
7-9	1.48	2.97	1.48	1.68	1.34	1.74	1.08	1.25	0.896	0.770
9-11	1.11	2.88	1.22	1.32	0.950	1.17	0.668	0.746	0.515	0.487
11-13	2.84	3.22	2.18	2.36	1.68	2.23	1.19	1.40	0.792	0.749
15-17	2.67	7.04	2.43	3.06	2.31	2.63	1.70	1.90	0.894	1.02
17-19	3.57	8.79	2.43	2.45	1.59	2.10	1.20	1.48	0.905	0.837
19-21	4.33	10.2	2.36	2.04	1.72	2.15	1.52	1.62	0.839	1.06
21-23	5.74	11.6		1.73	1.78	2.79	1.54	1.92	0.871	1.01
23-25	1.53	6.25	2.65	2.68	2.03	2.50	1.38	1.74	0.950	0.900
25-27	1.80	7.43	3.18	3.31	2.63	3.39	2.12	2.51	1.73	1.54
27-29	2.89	10.1	5.05	4.80	3.33	3.78	2.30	2.73	1.67	1.55
29-31	1.12	2.91	3.38	3.51	2.66	3.18	1.91	2.29	1.37	1.28
35-41	2.17	1.86	1.41	1.67	1.93	1.41	1.40	1.53	1.27	1.56

Interference from contamination.

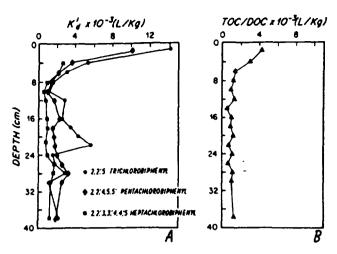


Fig. 3. (A) K'_4 profiles of three chlorobiphenyls. (B) TOC/DOC profile.

equilibrium with a truly dissolved phase. The concentrations of these two sorbed phases can be estimated by a knowledge of the appropriate $K_{oc}s$. We substitute for Eqn. (1) the following:

$$K'_{d} = \frac{\int_{oc} sK_{oc} sD}{D + \int_{oc} cK_{oc} cD}$$
 (2)

where f_{∞} and $f_{\infty}c$ are the mg of total organic carbon in a Kg of dry sediment and mg of colloidal organic carbon per liter of pore water, respectively, and K_{∞} and $K_{\infty}c$ are the sediment and colloidal carbon normalized partition coefficients. In the case where D is small compared to $f_{\infty}c$ $K_{\infty}c$ D, the expression reduces to:

$$K'_{\rm d} = \frac{\int_{\rm oc} s K_{\rm oc} s}{\int_{\rm oc} c K_{\rm oc} c} \tag{3}$$

Since K_{oc} and K_{oc} are not known for the compounds of interest, it is further assumed that colloidal organic matter has a sorption affinity similar to sedimentary organic matter for hydrophobic organic compounds. Studies with natural estuarine colloids indicate K_{oc} may be several times that of K_{∞} s although the slopes of the solubility dependence on Koc are identical (WI-JAYARATNE and MEANS, 1984a; MEANS and WIJAY-ARATNE, 1982). Unpublished, experimental studies in our own laboratory indicate that carbon normalized partition coefficients of PCBs with marine colloids are similar to those reported for freshwater sediments. Therefore, in the limit where most of the amount of PCB in pore solution is colloid-bound, an estimate of K_4 is simply the concentration ratio of organic carbon between sediment and colloidal organic phases: K'a $\simeq f_{\infty} s/f_{\infty} c$. In Fig. 3 we have compared the profile of TOC/DOC to that of K'_4 for a few PCB isomers. We assume that fec is reflected by the total DOC concentration. The similarity of the model K'd with those actually measured is surprisingly good, especially for the more highly chlorinated isomers.

The other major assumption in this model is that of equilibria between all three phases. There is contro-

versy in the literature involving hysterisis and reported "nonreversibility" of adsorption and desorption of hydrophobic organic compounds with sediments (DI TORO and HORZEMPA, 1982; GSCHWEND and WU, 1985). KARICKHOFF (1980) has shown that several sorbed PAH could be completely desorbed from sediments, but that the kinetics of desorption were slower than adsorption and that this rate could be modelled as a two step process. The rate of the slow, rate controlling, process decreased with increasing ring size and K_{∞} . The desorption rate constant for pyrene was as slow as 0.031 hr⁻¹. It is expected that the desorption rate for many PCBs could be considerably slower than pyrene and decrease as the degree of chlorination increases. It is not well understood how the organic content of the sediment and salinity of solution might affect adsorption-desorption kinetics. It is also not known how biological and chemical transformation and alteration of the sedimentary organic matter during diagenesis may affect the desorbability of sediment bound compounds. One further complicating factor is that there are dynamic interactions between sedimentary, colloidal and non-colloidal dissolved organic carbon. The nature and kinetics of these reactions are largely unknown. However, sediments, below the sedimentwater interface and in the absence of bioturbation, provide an environment where long time scale (years) equilibria can be approached and the extent of disequilibria minimized. In comparison, the overlying water column can be considered a much more dynamic and open system, where significant departures from equilibrium may occur.

The K'_d 's measured are chlorobiphenyl specific and tend to decrease with increasing degree of chlorination and decreasing solubility. Figure 4 shows the range and average K'_d as a function of the chlorine substitution (nCl) for three representative sediment sections. This trend is opposite of what is expected on the basis of solubility considerations. A strong inverse dependence of solubility on partitioning of PCBs is expected from laboratory results (KARICKHOFF et al., 1979;

164

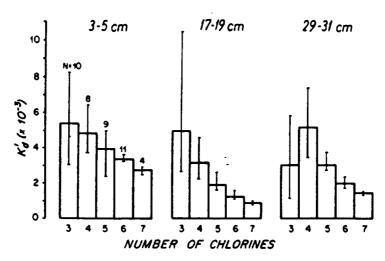


FIG. 4. Bar graphs of the mean K'_d as a function chlorine number for three representative depths. N equals the number of isomers or pairs of unresolved isomers considered and the bars represent the range of K'_d values determined.

SCHWARZENBACH and WESTALL, 1981; CHIOU et al., 1983) and has been observed in the water column measurements in the field (BOPP, 1979; PAVLOU and DEXTER, 1979). In contrast, it should be noted that EISENREICH et al. (1983) report no clear trend of K'_4 with increased degree of chlorination for PCBs in the water-column of Lake Superior. The lack of solubility dependence on K'_4 in our data is even more compelling evidence that the observed distribution is not simply two-phase sediment-water partitioning.

The enrichment in pore water of more highly chlorinated congeners relative to lesser chlorinated congeners is not easily explained. A diagenetic removal of tri- and tetrachlorobiphenyls occurring in pore water solution could explain their apparent depletion in pore waters if the desorption kinetics from the sediments are of similar time scales. Such processes still cannot explain the trends that occur with the penta- through heptachlorobiphenyls, which show no evidence of any removal. KARICKHOFF (1980) also found that the slow step in the adsorption rate decreased with molecular weight of the solute, and FREEMAN and CHEUNG (1981) have proposed a gel partition model for sorption in which the kinetics of sorption are diffusion controlled. Very slow adsorptive/absorptive approaches to equilibrium might explain the lower K_d s for the less soluble compounds. However, an examination of the K_{a} s for the range of chlorobiphenyls and for increasing depth in the core does not support the hypothesis of slow approach to equilibrium in this case. The K_4 of the trichlorobiphenyls does drop below that of the average tetrachlorobiphenyl in the bottom two sections. An explanation which is consistent with the results is that not all of the sorptive volume in the sedimentary organic matter is accessible to large hydrophobic organic compounds. If there is a steric hindrance to sorption sites, it might be expected that as molecular size increases with increasing nCl the effective volume of accessible sorbent organic matter decreases. This could

explain why colloidal organic matter, with its greater surface to volume ratio, apparently competes more effectively for larger chlorobiphenyls. Such a proposed mechanism needs to be tested, and may be specific for sediment type, type of organic matter in sediment, and appreciably influenced by interstitial water salinity and major ion chemistry.

Compositional changes of PCBs in the sediments

Compositions of PCB in many sediment profiles from the Hudson River estuary have been measured (BOPP, 1979; BOPP et al., 1981). There were only slight changes in peak ratios with depth, and those were directly attributable to changes in the up-river PCB source which was well documented. In contrast, there are marked changes in the composition of PCBs with increasing depth in our core. These changes in the sediments have been evaluated by looking at changes in in peak area ratios with depth. PCB no. 170 (2,2',3,3',4,4',5-heptachlorobiphenyl) was chosen as the reference compound, because it did not show apparent depletion relative to other PCBs, and is not expected to be readily biodegradeable, or be appreciably mobile in a dissolved form. The area ratio of each PCB to 170, A_1/A_{170} , has been calculated and profiles of this ratio normalized to that in the surface section have been generated. Examples of these profiles are seen in Fig. 5. The relative concentrations of the di- and trichlorobiphenyls decrease faster than the tetrachlorobiphenyls and the relative concentrations of the penta-, hexa- and heptachlorobiphenyls remain essentially constant. The extent of the depletion is isomer specific within the di-, tri- and tetrachlorobiphenyls. The relative depletions of some of the chlorobiphenyls are striking. The major peak in Aroclor 1242 is an unresolved mixture of isomers 28 and 31. The relative concentration of this peak is depleted at 35-41 cm to 2.2% of that in the 0-3 cm section (Fig. 5). 2,3,4'-trichloro-

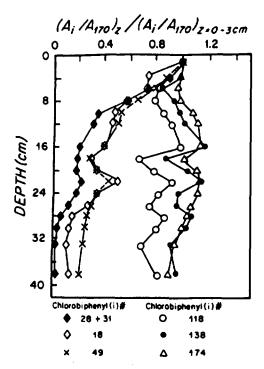


FIG. 5. Profiles of the area ratios of individual chlorobiphenyls (i) in the sediments to 170 normalized to the ratio measured in the surface sediment (Z=0-3 cm). The structures of the chlorobiphenyl *s are given in Table 2.

biphenyl (chlorobiphenyl no. 22) is similarly depleted to 1.4% of its surface ratio. Variations in the relative concentrations of penta-through heptachlorobiphenyls are small.

The relative concentrations of most of the di-, tri-, and tetrachlorobiphenyls decrease as smooth profiles with local maxima at 21-23 cm. Note that these maxima in relative concentration of many chlorobiphenyls correspond to a minima in the C/N ratio and to local maxima in organic matter and water contents. These changes may be a function of either a change in the source or type of sediment or past injection of relatively fresh sediment from above into these depth horizons by the activities of large burrowing organisms. Visual observations and interstitial water sulfate does not indicate evidence of recent large scale burrowing.

Processes which need to be considered in evaluating compositional changes are: 1) changes in the source of PCBs to the sediment bed over time, 2) migration, via diffusion or advection of PCBs in the interstitial water, 3) chemical transformations, and 4) biological degradation of PCBs. BOPP et al. (1981) have suggested that changes in suspended particle concentration with time and subsequent deposition can result in changes in PCB composition with depth, with the less soluble chlorobiphenyls being enriched in times of high suspended loads. However, source changes of PCBs are unlikely to explain the major features of our profiles. Aroclor 1242 type mixtures are changed dramatically as the major chlorobiphenyls are nearly completely depleted

in the bottom sections of the core. The composition of Aroclor 1254 remains relatively unchanged except for the tetrachlorobiphenyls. The smooth, chlorobiphenyl specific nature of the depletion profiles within both formulations, and near constant ratios of pentathrough heptachlorobiphenyls argues against abrupt changes in the source of PCBs to the sediment. Other sediment samples and a core from the inner harbor show compositions similar to those in the surface sediment here, and compositional changes with depth have not been observed (BROWNAWELL and FARRINGTON, 1985).

Migration of hydrophobic organic compounds in sediments has not been satisfactorily studied. Diffusion of sediment bound PCBs is impeded by sorption and their high K'as. The mean distance that a particle tracer will migrate in the sediment can be estimated by VD'I (BERNER, 1976) where D' in this case can be estimated by $D_a/1 + K'_a$, where D_a is the sediment diffusion coefficient of solute in seawater corrected for sediment tortuosity. Assuming a D_s of 10⁻⁶ cm²/sec for a dissolved PCB, a K'4 of 103, and that the sediment profile represents about 20 years, then the mean distance that a PCB particle tracer will migrate is 0.79 cm. Pore water advection could be a more effective way to mobilize PCB in sediments, but the salinity shows no evidence of appreciable groundwater advection at this site. However, seawater can advect without salinity changes. If advection or diffusion were controlling the solid phase concentrations to any extent. it would not be expected that the composition of the higher molecular weight isomers would remain so constant, as these isomers are enriched in pore water solution in ratios unlike that of the sediment. The migrational properties of colloidal organic matter and associated sorbates will be different than that of dissolved solutes. Diffusion of hydrophilic organic colloids may be much less impeded by sorption than that of dissolved PCBs. The role and migrational properties of organic colloids in sediments need to be better understood to critically evaluate remobilization of hydrophobic organic compounds in sediments.

Rapid rates of degradation of several chlorinated hydrocarbons have been observed in reducing environments. Reductive dehalogenation appears to be the main pathway and converts DDT to DDD (GLASS, 1972; ZORO et al., 1974), DTE to DDE (BELAND et al., 1974), and lindane to benzene (BELAND et al., 1976) under reducing conditions. Anaerobic degradation to toxaphene mixtures has also been reported in anaerobic soils (PARR and SMITH, 1976) and in salt marsh sediments (WILLIAMS and BIDLEMAN, 1978). These and other papers dispute the role of biological processes in this mechanism. ZORO et al., (1974) argue that the reduction is purely chemical and that reduced iron porphyrins may be important in catalyzing this reduction in nature. The reduction potentials of chlorinated hydrocarbons are an indicator of whether a compound can break down in this manner. BELAND et al. (1976) state that as a rule organochlorine compounds with a

first reduction potential (E_{2d}) more positive than -1.521 V versus a saturated calomel electrode will reductively dehalogenate under strongly reducing conditions and those compounds with an E_{24} less than -1.757 V will not. E_{2d} values ranging from -1.771 to -2.126 V have been reported for several chlorobiphenyls which can exist in industrial formulations of PCB (FARWELL et al., 1973). The ease of reduction tends to increase with increasing number of chlorines, which is opposite of the trend reported in the chlorobiphenyl depletions noted here. Brown et al. (1984) have noted decreases of highly chlorinated biphenyls in highly contaminated sediment cores from the upper Hudson River. Increases in mono- and dichlorobiphenyls not present in Aroclor mixtures were also observed. These workers suggest that PCBs were reductively dechlorinated by anaerobic bacteria, because chemical reductants are not known for PCBs at environmental levels. Recent results (SULFITA et al., 1983) demonstrate microbial dehalogenation of haloaromatic substrates by strict methanogens in culture.

Aerobic microbial degradation of PCBs has been extensively studied with both mixed and pure cultures. Susceptibility to, and rates of degradation are seen to be chlorobiphenyl specific and depend on both the number and substitution of chlorines. SHIARIS and SAYLER (1982) and BAILEY et al. (1983) showed degradation of monochlorobiphenyls by natural assemblages of freshwater microorganisms but none for higher chlorinated congeners. CAREY and HARVEY (1978) found small amounts of degradation of 2,2',5-trichlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl in experiments with marine bacteria but not degradation in experiments which were performed anaerobically.

The primary mechanism of degradation in pure culture studies involves dioxygenase attack preferentially at the 2',3'-positions (FURUKAWA et al., 1979; MASSE et al., 1984). The major pathway of degradation of many PCBs is postulated to proceed through formation of the 2'3'-dihydro-diol compounds, reduction to the corresponding 2'3'-diols, which are then cleaved by meta fission at the 1'2' position to the 6-oxo-dienoic acids and finally to the chlorobenzaoic acids. FURU-KAWA et al. (1978) report the rates of biodegradation for 31 chlorobiphenyls by species of Alcaligenes and Acinetabactor. Relative rates of degradation by both species generally decrease to very low rates for the tetraand pentachlorobiphenyls. The relative rates of degradation within the trichlorobiphenyls reported is quite similar to the relative degrees of isomer depletion in the sediment profiles. The reported degradation rates for 2,4,4'- and 2,4',5-trichlorobiphenyls are between 6 and 25 times faster than for 2,2',5-trichlorobiphenyl. The same relationship in the depletion profiles of these isomers is seen in Fig. 5. Chlorine substitution factors which influence the rate of degradation are complicated and can be related to the number of active sites or vicinal hydrogens available, field effects which will stabilize electrophilic attack (particularly at the 2.3 vicinal hydrogen positions), and steric effects which can also effect the planarity of the biphenyl molecule.

The specificity and relative rates of chlorobiphenyl depletion in our core seem to be consistent with the pattern expected for microbial diagenesis. However, this site is very reducing and microorganisms would not be able to use the oxidative pathways outlined above. Sporadic introduction of oxygen by burrowing organisms is an unlikely explanation given the smooth profiles extending to 41 cm. Some type of microbially mediated electrophilic degradation would explain our observations. However, the nature of the populations, and the mechanisms of transformation are not understood.

GENERAL DISCUSSION

We suggest that the data for this core coupled with other data from the literature support our hypothesis that the biogeochemistries of PCBs in the interstitial waters of this core were largely affected by an association of PCBs with organic colloids. Interactions of PCBs and other hydrophobic organic compounds with organic colloids will influence remobilization rates of these compounds in sediments and are likely to affect rates of diagenetic transformations. The quantitative role of organic colloids will depend on the quantity and quality of organic matter in the sediments as well as physical chemical properties of the compound of interest. Profiles of interstitial water PCBs indicate a diffusional flux to the overlying water column. However, uncertainties concerning the migrational behaviour of colloids and the importance of mixing processes within the sediments prevent reasonable calculations of this flux. Consideration of these processes is necessary in calculating residence times of many organic compounds in sediments. Further studies should also be aimed at developing a better understanding of the role of organic colloids in the bioavailability of hydrophobic organic compounds that are known or potential xenobiotic compounds.

CONCLUSIONS

- 1) Highly elevated concentrations of PCBs are reported in the interstitial waters of an organic rich coastal sediment from New Bedford Harbor. Evidence has been presented to suggest an important role of organic colloids in the biogeochemistry of PCBs in this sediment. Several lines of evidence indicate an association of PCBs with colloids in interstitial waters:
- a) PCB concentrations increase with depth to supersaturated levels for many chlorobiphenyls. This increase correlates with the DOC profile.
- b) K'_d decreases with depth in the sediment for all of the chlorobiphenyls measured. The magnitude and shape of the K'_d profiles can be modelled reasonably well assuming three-phase equilibria where the dissolved phase is small compared to the colloidal phase.
- c) The compositions of chlorobiphenyls in pore water solution and the reverse trend in the K'_d with nCl's are not that expected in a 2-phase, solid-solution partitioning situation. An important colloidal phase needs to be invoked to explain these distributions.

- d) The results from relevant laboratory studies would indicate that a high percentage of PCBs that are in pore water solution will be sorbed to organic colloids at the level of colloids which probably exists here.
- 2) Isomer specific depletions of di-, tri- and tetrachlorobiphenyls were observed with increasing depth in this core. This is probably the result of microbial degradation of PCBs at this site, although the lack of oxic conditions requires the presence of microbial degradation pathways yet to be characterized.
- 3) These results indicate that a greater understanding of partitioning of hydrophobic organic compounds with organic colloids is necessary in evaluating the mobility and bioavailability of these compounds in sediments.

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